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BASIC OPEN-HEARTH SLAG CONTROL

BY EARNSHAW COOK

Abstract

The history of the development of slag oxidation control and its application to the basic open-hearth operation is described. The physical chemistry of the process is discussed in detail. Theoretical burden calculations are presented with reference to variations of the materials charged and to the blast furnace open-hearth balance of manganese and phosphorus. A detailed abstract is available in the final summary of the research.

INTRODUCTION

INTRODUCTION to the intricacies of modern open-hearth operation has changed materially from the pioneering days not many years ago when the mysteries of steel melting were jealously guarded for the benefit of the initiated, and improvements of practice were discovered principally by a strenuous experience to which modern industry owes an unfailing debt of gratitude. Through the enlightenment of chemical and metallurgical research extending over the last three decades, together with the rise of technically-trained men to positions of importance in the field, much of this reticence has disappeared in favor of the idea that a closed-shop policy excludes more valuable information than it is able to withhold. Accurate knowledge of high temperature metallurgical reactions has been and yet remains so restricted that operatives usually welcome an opportunity to compare notes and experience concerning various practices in anticipation of mutual advantages occasioned by the exchange. Steel making may never be reduced to an exact science, but there is a satisfactory, slowly-developing tendency for the practitioner to establish both methods and opinions upon the best available metallurgical observations based on average results obtained over a representative cross-section of the operation.

While the innumerable variations of the raw materials and those peculiar to the operation itself combine to defeat close technical con-

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trol and relegate steel refining to the realms of necromantic art, nevertheless, gradually accumulating evidence promotes the opinion that the highest skill of the melter must be primarily concerned with a three, possibly four, dimensional combination of time, temperature, concentration and pressure so co-ordinated as to obtain the most favorable conditions of bath temperatures and slag analyses for the particular preliminary steel analysis required by the chemical specifications and followed by deoxidation measures varied according to relative bath oxidation for either rimmed or killed steel.

This paper is principally concerned with reduction to actual operating practices of sundry findings in the field of metallurgical control developed over the past ten years in the basic open-hearth. These phases of steel manufacture are so intimately related that discussion of any particular variable necessarily involves a working knowledge of all the others. Thus, for example, the more obscure problems of refining may be best approached after the operating and research personnel has been carefully trained and regularly supervised in the standardization of tapping, pouring and rolling temperatures of the product. Tonnages outside reasonable variations of the temperature schedules may not be properly included in the comparison of results which might otherwise be unduly influenced by thermal effects. Every metallurgical investigation must exercise the utmost care in the selection of data for statistical comparisons lest preconceived ideas, inaccurate observations, obscure or hidden variables, non-representative evidence or any of the other countless misconceptions possible serve to obscure the issue and promote erroneous or premature conclusions.

RÉSUMÉ OF EARLY LITURATURE

Both metallurgical and petrographic researches upon basic open-hearth slags have received considerable attention from British and German investigators from the beginning of the Siemans-Martin process. One of the earliest commentaries upon this subject is included in that remarkable volume on the "Manufacture and Properties of Iron and Steel" (1)¹ by H. H. Campbell and which is here reproduced in its essential parts:

"The proportions of SiO_2 and CaO are the main points in a basic slag, but other factors exercise an important influence upon the

¹The figures appearing in parentheses pertain to the reference appended to this paper.

result. Magnesia is always present from the wear of the hearth, but is undesirable, as it makes the slag viscous and has less power to hold phosphorus than lime. Alumina comes from the impurities in the dolomite, lime and ore, but being usually in small amount may be neglected. Manganese is usually present in the stock and serves a useful purpose in conferring fluidity upon the slag. It is also valuable in removing sulphur by the formation of sulphide of manganese, which floats to the top of the metal, where the sulphur, being exposed to the flame, is oxidized and passes away with the waste gases. This action is uncertain, and the explanation is somewhat a matter of supposition, but it seems well proven that manganese, either metallic or in the form of ore, aids in the elimination of sulphur, and the above theory is in accord with the purification of pig-iron by the addition of spiegel.

"All the components enumerated are fixed and determined agents in the transactions. Manganese is sometimes reduced from the slag by the carbon of the bath, and a certain percentage may remain unoxidized in the metal, but aside from this the oxides of aluminum, silicon and manganese exist in the slag in just the quantities that were added with the stock; but there are three other constituents—iron oxide, phosphoric acid, and sulphur—whose presence in the slag is determined by the conditions of manipulation and by the proportions of other constituents. Iron oxide is always present, the exact amount depending upon the reducing power of the carbon of the bath. It matters not whether ore is added before melting, after melting, or not at all; there is a certain content of FeO which is demanded by existing conditions, and that certain content will be present. An exception must be made in the case of ore added after the carbon is nearly eliminated, but aside from this there will be just as much iron oxide lost in the slag when no ore is used as when it has been added in proper quantity, and, therefore, all the ore is clear gain.

"In the basic process there is difficulty in making a slag entirely of silicate of lime, for this is more viscous than a slag of the same percentage of silica containing other bases; there is a tendency, therefore, toward the absorption of iron oxide, but this is opposed by a contest on the part of the lime for the possession of the silica, and the result is a decrease in the percentage of iron when there is an increase in lime. Inasmuch as the substitution of CaO for FeO produces a more viscous slag, this would seem to invalidate the theory just advanced, but the effect is due not to a change in the law, but

to the action of stronger forces. The more bases present, the less necessity is there for an additional amount, since the weight of silica necessarily remains constant, and, as the reducing action of the metalloids comes into play, the slag begins to be robbed of its iron, which at the time is its most reducible and its most fusible base. The presence of oxide of manganese in the slag modifies without completely changing the relations just described, for, by furnishing an additional base and imparting greater fluidity, it tends to render the presence of iron oxide less necessary.

"Fluidity is of vital practical importance, for the slag must run freely from the furnace, else the hearth will soon be filled; furthermore, the slag must be so basic that the hearth is not scorified.

"The two conditions, fluidity and basicity, determine the nature and amount of the basic additions, for the sum of CaO and MgO cannot much exceed 55 per cent without producing a viscous cinder, neither can the percentage of SiO_2 fall below 10 per cent, unless unusual amounts are present of the oxides of iron, manganese, or phosphorus. This theory of the automatic regulation of fluidity seems to account for a curious relation between the content of SiO_2 and FeO in a large number of basic slags, which are grouped in Table XI-D.

"The phosphoric acid was not determined, but it may be taken for granted that an increased proportion of phosphorus in the charge will give higher phosphoric acid in the cinder, and the table shows that in the case of high phosphorus, the combined SiO_2 and FeO runs about 27.5 per cent, with medium phosphorus about 35 per cent and with low phosphorus about 36 to 37 per cent. A difference in manipulation would change the absolute percentages, but the attainment of a certain definite content of $\text{FeO} + \text{SiO}_2$ seems assured. This conclusion is verified by the examination of the individuals of the original records, for it is found that low SiO_2 is accompanied by high FeO , and vice versa. This is shown by Table I, which is composed of the extreme cases of high and low percentages of SiO_2 and FeO , the individual heats which compose the groups in Table XI-D.

"It would be wrong to suppose that an increase in SiO_2 has reduced the FeO by simple dilution, for a reduction in FeO from 20 per cent to 10 per cent would imply a permanent addition of SiO_2 equal to the entire volume of the slag, and this is absurd. The conclusion seems inevitable that SiO_2 and FeO replace one another in some way, and that one fulfills some function of the other. As FeO is basic and SiO_2 is acid, this function cannot be related to the

basicity of the slag, and the only explanation which suggests itself is that both confer fluidity and that there is an automatic regulation of this quality in accordance with the theory before elaborated."

Table I
Relation Between Silica and Iron Oxide

Initial phosphorus in charge, per cent	Slag showing maximum SiO ₂ per cent		Slag showing maximum FeO per cent	
	SiO ₂	FeO	SiO ₂	FeO
1.35	16.50	6.99	9.46	27.72
0.19	27.35	6.63	9.53	34.47
0.10	29.15	8.27	15.66	34.36

Among the first petrographic combinations of slags was the publication of J. H. L. Vogt (2) in 1885 in which observation of the following minerals was reported:

Name	Formula
Augite	Ca (MgFe) SiO ₃
Enstatite	MgSiO ₃
Wollastonite	CaSiO ₃
Melilite	(Ro) ₁₂ (Al ₂ O ₃) ₂ (SiO ₂) ₉
Monticellite	CaMgSiO ₄
Gehlenite	(Ro) ₃ (Al ₂ O ₃) (SiO ₂) ₂
Spinel	Ro.R ₂ O ₃
Fayalite	(MnFe) ₂ SiO ₄
Magnetite	FeO.Fe ₂ O ₃
Olivine	MgO.FeO.SiO ₂

It was suggested that "sulphur in slag always appears as a constituent of monosulphides crystallizing in the isometric system; CaS, MnS, FeS. The pyroxine minerals with the hexagonal lime silicate only separate out from fused masses that contain a larger percentage of silica than that indicated by the oxygen ratio of 1:1.50/1.60 while with a smaller percentage of silica, olivine separates out."

Wilson (3) proceeded to further elaborate the Campbell viscosity theory of basic slags which he classified as follows:

1. The Olivine Type: 2Ro . SiO₂
2. The Mellilite Type: 3Ro . SiO₂

"Ideal viscosity" is described as the degree at which the slag would in actual furnace practice be considered as between a "thick" and "thin" condition. When a molten slag departs from the ideal constituency, certain reactions take place whose influence is to return it quickly to the ideal point. Given constant temperatures, these

balancing reactions are supposed to so change the slag composition that the viscosity will approach the ideal degree.

"The resultant of this automatic balance is considered as due to two separate sources:

1. The reduction from the slag to the metal of such elements as impart increased fusibility to the slag. The oxides of iron, manganese and phosphorus are the most important compounds so reduced.
2. Chemical action with the banks, the outcome of which will be to bring compounds of CaO and MgO into the slag to make it less fusible."

All slags are further suggested by Wilson to so balance themselves as to become chemically inert. By the first inert stage is meant the composition at which the slag will be still inert and yet contain the highest proportion of acids possible in a normal steel furnace slag. After this point, as the slag becomes more basic, the inert condition is attained when the viscosity reaches the ideal degree. If the viscosity exceeds the ideal, the change in slag composition will be brought about by the passage of such oxides as those of Fe, Mn and P from the metal to the slag. As reported by Stead, the probability is that FeO can act as an acid and combine with CaO in steel furnace practice at comparatively low temperature.

Wilson asserts that the composition of tapping slags should be such that the purification of the steel is brought to a satisfactory degree and the temperature to a sufficiently high point in the most economical manner and by the least expenditure of bases. He has unfortunately neglected to describe either the exact theory or practice to be adapted for the attainment of this desirable state of affairs.

A detailed study of the possible mineral compounds present in basic open-hearth slags was contributed by Von Jonstorff (4) in 1920. He remarks that Ledebur was among the first to consider steel slags as an inter-oxide solution rather than as complicated chemical compounds: All constitutions of slags and especially those of metallic oxides of silicon, phosphorus, etc., occur together in quantities which vary extremely and are without regular laws of combination. Hence it follows that slag need not consist of a single compound but is to be viewed as a solidified solution in one another of different chemical compounds. That definite compounds may form in the fluid and solid slags is not to be doubted but these only become recognizable when the slag solidifies or subsequently.

Von Jonstorff divides slags into three groups:

1. Silicate slags of metallic oxides and silica.
2. Phosphate slags of metallic oxides and phosphoric acid.
3. Oxide slags of essentially metallic oxides.

In metallurgy, the paper continues, "a series of formulae is usually employed as shown in the following table:"

Oxygen Ratio (A/B)	Description	Molecular Form	
		Monoxide Base	Sesquioxide Base
0.67	Subsilicate	$3\text{Ro} \cdot \text{SiO}_2$	$\text{R}_2\text{O}_3 \cdot \text{SiO}_2$
1.00	Monosilicate	$2\text{Ro} \cdot \text{SiO}_2$	$2\text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$
1.50	Sesquisilicate	$4\text{Ro} \cdot 3\text{SiO}_2$	$4\text{R}_2\text{O}_3 \cdot 9\text{SiO}_2$
2.00	Bisilicate	$\text{Ro} \cdot \text{SiO}_2$	$\text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$
3.00	Trisilicate	$2\text{Ro} \cdot 3\text{SiO}_2$	$2\text{R}_2\text{O}_3 \cdot 9\text{SiO}_2$

Vogt is quoted in an important observation to the effect that the existence of minerals in the molten mass distinctly depends on the average chemical composition and that their formation depends principally upon chemical mass action.

It is Von Jonstorff's opinion "that the very basic slags are characterized by sesquioxide compounds such as spinel, $(\text{RO} \cdot \text{R}_2\text{O}_3)$, which crystallizes out before the silicates and occurs only up to 2.00 acid oxygen ratios. In fused matrices which contain both FeO and Fe_2O_3 , magnetite forms very readily and ferric oxide may also combine with other compounds."

In 1923 the influence of FeO slag concentrations upon bath oxidation was discussed in great and abstruse detail by Styri (5) with little reference to intermolecular slag reactions but in a manner which may well have inspired subsequent investigations toward the application of physical chemistry to the chemistry of open-hearth reactions.

One of the most interesting and valuable researches upon the general subject was published by Colclough (6) in 1923. To do it proper justice, the paper should be reproduced in full for it assuredly merits the careful examination of all serious students of the problem. The findings are here abstracted as faithfully as possible.

"The study of slags produced in the manufacture of basic steel has proceeded mainly along two lines:

1. Petrographic investigation of the mineralogical constituents of the solidified material in the endeavor to identify the compounds present. This method is unsatisfactory because there is little or no direct evidence to show whether the compounds found had any existence in the liquid slag or have

been merely formed by selective crystallization during freezing.

2. The alternative method is to take samples of slag under stable conditions in the furnace and to endeavor to allocate chemical compositions to the constituents found. This procedure where slag samples are taken alone appears to be unsound: the nature of the slag present on the surface of the metal is certain to vary according to the properties of the bath with which it is in contact and, therefore, requires that slag and metal must be considered together.

By studying the relative ratios of elimination of various elements in respect to slag composition, Colclough proceeds to a concept of the reactions and of the nature of the products. "The oxide of iron formed during melting first removes the whole of the silicon from the metal; the resulting silica forms, with the lime, the basis of the slag. The surplus oxygen from this preferential oxidation attacks the phosphorus in the bath up to a definite limit; beyond this it oxidizes the carbon and manganese.

"From tabulations of melting slags and corresponding steel analyses Colclough shows that each molecule of phosphoric acid is associated with four of lime, while each molecule of silica requires two of base which may be either CaO , MgO , MnO or to a small extent, FeO . This series therefore supports the accepted opinion that the fundamental slag in a basic open-hearth furnace is essentially composed of molecules of phosphate of lime ($4\text{CaO} \cdot \text{P}_2\text{O}_5$) and molecules of monosilicate ($2\text{RO} \cdot \text{SiO}_2$). If the metal possesses a high silicon content while the lime added be small, the bath at melting will have a high phosphorus content and vice versa.

"Tests made show that if the silicate be free from oxide of iron, the fundamental slag is quite stable and can be maintained in the presence of the reducing elements, carbon and phosphorus. The addition of further oxide of iron to the slag does not appear to have any direct effect on its constitution beyond the solution of the oxide. If lime be added to a melting slag, a fundamental change takes place in its composition. It appears that manganese silicate is unstable in the presence of free lime. As a result the lime added tends to replace manganous oxide in the silicate to form the simple compound $2\text{CaO} \cdot \text{SiO}_2$ and free MnO .

"That a change occurs in the state of the oxide of manganese is shown by the fact that so long as lime is not added, the manganese content of the bath either remains constant or falls slightly, while on

the addition of lime there is an instant reduction of manganese to the bath.

"With the addition of more lime than is necessary with MgO to combine with the whole of the P_2O_5 and SiO_2 present, it is probable that the excess lime forms a fairly stable compound with ferric oxide. In view of the fact that Fe_2O_3 is not the stable form of iron oxide at steel making temperatures, particularly in the presence of metal rich in oxidation elements, one is driven to the conclusion that the ferric oxide must be present as some fairly stable compound such as calcium ferrate ($x \text{ CaO} \cdot \text{Fe}_2\text{O}_3$) as prepared by Stead and others.

"While Colclough made no experiments with tapping slags because of the difficulty of keeping the bath under control, he ventured the opinion that in order to prevent any danger of the return of phosphorus to the metal, the slag should be a mixture of calcium phosphate and monosilicate of lime with the other constituents in solution. The amount of phosphorus oxidized depends entirely upon the amount of oxide of phosphorus that the slag can hold and this in turn is fixed by the excess base above that required to form a monosilicate with the SiO_2 present. If oxide of iron is added to a true melting slag, the basicity is not increased, no more phosphorus can be absorbed and the whole of the added oxide is free to oxidize the carbon of the metal even in the early stages of the heat and in the presence of phosphorus.

"The various tabulations included in the experimental data indicate that there is a minimum critical value for the basicity of a slag below which no further oxidation of phosphorus can occur. If lime be added to such a slag, the oxidation of phosphorus and carbon proceeds simultaneously. When, however, the slag approaches a second critical composition where there is sufficient CaO of itself to form the phosphate and monosilicate of lime, phosphorus having the highest heat of oxidation is eliminated alone with no drop in carbon and reduction of both FeO and MnO from the slag. The oxidation of phosphorus then slows down by virtue of its low concentration and the oxides become available for the carbon and manganese.

"In the basic process the oxidation of manganese is far less rapid than for acid practice; migrations of manganese between metal and slag have been the subject of many investigations. Naske comes to the conclusion that the distribution of manganese between metal and slag depends upon the relative concentrations of MnO and FeO in the slag: if the ratio of MnO to FeO exceeds unity, reduction of

MnO is brought about. Dichman suggests that the reduction of MnO depends upon the total concentration of oxidizing elements in the slag and that it occurs whenever the FeO falls below 12 per cent.

"It would appear according to Colclough that the distribution of manganese depends upon two factors:

1. Whether the MnO is in the free state or combined with silica.
2. Upon a balance of the several reactions between manganese and iron oxide, and manganese oxide with phosphorus and carbon.

By virtue of its greater heat of formation, phosphorus oxidation will, other conditions favorable, be preferential and formation of MnO will follow. The net distribution of manganese between slag and metal will depend upon the difference in the velocity of the reactions and could not be covered by any sort of simple ruling.

"Examination of the data suggests to Colclough a remarkable parallel between the behavior of the manganese in the charge and the elimination of sulphur. In all cases where the lime content (and therefore the basicity) was low, there was a general oxidation of manganese and no elimination of sulphur. On the other hand, whenever spar and lime were added, the basicity of the slag increased while the iron oxide content was low, there was a reduction of MnO to the bath and the removal of sulphur invariably followed. This manganese added to the bath is the active agent in the removal of sulphur, MnS passing into the slag and being converted into MnO and SO₂ which passes away in the chimney gases. If conditions remain favorable, the MnO is reduced and the cycle of operations continues.

"A summary of the conclusions contained in Colclough's paper follows:

1. The slag formed in a basic open-hearth furnace is essentially 4CaO.P₂O₅ with the monosilicate of CaO, MgO and MnO.
2. The addition of acid oxides causes instability and obtains return of phosphorus to the metal.
3. Additions of basic oxides merely pass into solution and the type of compound is not altered. In certain cases there is probably a compound of lime and ferric oxide formed which is comparatively stable.
4. When an excess of lime is present, MnO is carried

in solution and under certain conditions is reducible to manganese.

5. The relative ratio of oxidation of carbon and phosphorus depend primarily on the basicity of the slag and there are two critical compositions:

(a) When the total bases are sufficient only to form the fundamental slag (1), there is no further oxidation of phosphorus and carbon is eliminated.

(b) When the lime content is sufficient of itself to form the silicate and phosphate, the carbon remains constant until nearly all the phosphorus is eliminated.

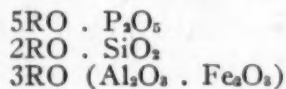
6. The removal of sulphur is only indirectly due to the presence of a high lime content; the direct agent is manganese which is thrown into the bath from the slag."

J. E. Fletcher, (7), in correspondence on the above paper which he highly commended, suggested that "while the bulk of such slags would be a phosphate of the type $n\text{RO} \cdot \text{P}_2\text{O}_5$, the value of 'n' for molten slags had not yet been determined with certainty. He had strong ground for the belief that these slags tended towards the inert condition where the ratio of acid to basic oxygen was unity as commonly attained in puddling slags considering Al_2O_3 and Fe_2O_3 as acid oxides.

"It was generally agreed that the neutral silicate $2\text{RO} \cdot \text{SiO}_2$ was present and Fletcher had occasionally found soaking pit slags very closely represented by the $3\text{FeO} \cdot \text{Fe}_2\text{O}_3$ type which was again of neutral character. His own investigations led him to believe that as the tendency in both steel and puddling processes was toward the neutral balance, the critical points alluded to by the author occurred when the slag approached that condition.

"The phenomenon of CaO replacement of MnO in the $2\text{RO} \cdot \text{SiO}_2$ constituent was important but the reduction of manganese to the metal only occurred when the slag was acid,—that was when the acid oxygen content in P_2O_5 , Al_2O_3 and Fe_2O_3 was greater than the basic oxygen content in CaO , MgO , MnO and FeO .

"This contention supported by Dichman and Von Jüptner was substantiated if the slags were considered as consisting of the three neutral constituents:



with free SiO_2 if acid and RO (FeO or CaO) in solution if basic. The total basic oxygen content was a critical function and influenced the rate of phosphorus elimination from the metal in direct proportion to the percentage of acid oxygen content in the phosphate and silicate constituents. This was stated to bear out H. H. Campbell's discovery that rephosphorization occurred in basic open-hearth slags if the sum of the oxygen contents of SiO_2 and P_2O_5 exceeded the following figures:

Per Cent P_2O_5	Per Cent Oxygen in $\text{SiO}_2 + \text{P}_2\text{O}_5$
5	13.5
10	15.0
15	16.5
20	17.5

A most interesting and able paper published by Herty (8) in 1926 on the chemical equilibriums of manganese, carbon and phosphorus in the basic open-hearth offers the following conclusions:

"1. The amount of residual manganese excepting where the slag contains over 5 per cent P_2O_5 , is controlled by the total manganese charged, the amount volatilized, the iron oxide content of the slag, the basicity of the slag, the slag volume and the temperature.

2. The quantitative relationship between these variables, excepting volatilization is:

$$109 K_{\text{Mn}} = \left(\frac{10^5}{T} - 28.25 \right) \frac{1}{5} = 0.053 \text{ (2925 Degrees Fahr.)}$$

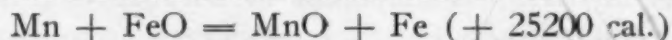
Where

$$K_{\text{Mn}} = \frac{(\text{MnO}) (\text{Available Base})^{0.5}}{(\text{Mn}) (\text{FeO})}$$

The slag concentrations are expressed as mols per 100 weight units and the metal, as weight per cent; temperature equals degrees Fahrenheit, absolute.

The available base is calculated as the excess mols of CaO above that necessary to form $\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{P}_2\text{O}_5$.

3. From a consideration of the heat of the reaction



as calculated from plant data and from heats of formation at room temperature, the solubility of FeO in the metal increases 1.25 times as fast as that of MnO for a given increase in temperature.

4. The amount of iron oxide in the metal is not controlled by the residual manganese present but by both manganese and MnO since the ratio $\frac{\text{MnO}}{(\text{Mn}) (\text{FeO})}$ must be constant for a given temperature. Since the concentration of Mn in the metal depends on that of MnO in the slag, it is possible to have the same concentration of FeO in the metal with 0.10 per cent Mn as with 0.40 per cent Mn, provided only that the amount of MnO in the slag is four times as high in the second case as in the first.

Residual manganese does not, therefore, serve as a protector against oxidation of the metal although high residual manganese may denote a bath low in iron oxide. The low iron oxide in the bath is the agent for, and not the result of, high residual manganese.

5. The amount of carbon in the metal depends upon the concentration of iron oxide in the slag and on the temperature.

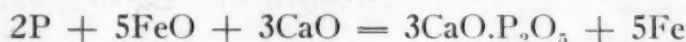
6. The amount of phosphorus in the metal depends on the total phosphorus in the charge, the iron oxide content of the slag, the basicity of the slag, the slag volume and temperature.

7. Where concentrations and temperatures are expressed as in paragraph 2, the quantitative relationship between the above variables is:

$$109 (K_p \times 10^{-5}) = \frac{P_2O_5}{(P)^2 (FeO)^5 (CaO)^3} = 0.620 \text{ (2925 Degrees Fahr.)}$$

$$= \left(\frac{10^5}{T} - 28.52 \right) \frac{1}{1.322}$$

8. The heat of the reaction



is plus 209,000 calories per mol.

There appears in Bulletin 34 (9) of the Carnegie Institute of Technology and the U. S. Bureau of Mines a detailed discussion of the physical chemistry of steel making which is of general interest. It is stated that "the oxidation of metalloids in the basic open-hearth is carried out by the following reactions:

1. *Carbon*—The reaction for the carbon elimination is:



The reaction absorbs heat and is favored by high temperatures.

2. *Silicon*—Silicon is oxidized very rapidly by the reaction:

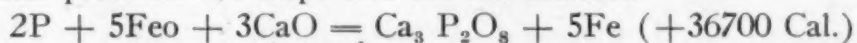


This reaction is exothermic and is promoted by lower temperatures. Almost all the iron oxide formed by oxidation of the charge will be removed by the silicon thereby tending to slow down the elimination of carbon if ore is not charged.

3. *Manganese*—This element reacts with iron oxide as shown by $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe} (+25100)$

The reaction is exothermic and manganese is usually eliminated rapidly after the addition of pig iron.

4. *Phosphorus*—The elimination of phosphorus probably takes place in two steps and the net reaction



is exothermic and is favored by low temperatures. For this reason phosphorus is usually eliminated rapidly immediately after the addition of hot metal provided that there be sufficient iron oxide and not too much silica in the slag.

5. *Sulphur*—The elimination of sulphur is retarded by high iron oxide slags. The fundamental reaction is



and being almost neutral as regards heat effects is nevertheless favored by high temperatures. Inasmuch as open-hearth slags are almost always highly oxidizing it can be readily seen that the amount of sulphur eliminated must be necessarily small unless use is made of special slags which are strongly basic and weakly oxidizing.

“Three of the most important problems in open-hearth practice require a knowledge of the solubility of iron oxide in the bath:

1. The speed of operation of the furnace depends for a given charge and combustion conditions on how fast the iron oxide will diffuse from the slag into the metal. The rate of diffusion depends upon the viscosity of the slag, the temperature, the amount of iron oxide in the metal and the solubility of iron oxide in the metal under open-hearth slags.

2. The amount of oxygen in the steel before deoxidation depends upon the carbon content of the metal and the temper-

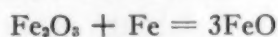
ature. If the heat is brought to the finishing condition slowly the iron oxide in the bath will be essentially in equilibrium with that of the slag and in this case the carbon in the metal will be in equilibrium with the iron oxide in the slag. If the heat is worked rapidly the carbon will be in equilibrium with the iron oxide of the metal but not of the slag. Knowledge of the equilibria between slag and metal will show how much carbon might be lost under any slag.

3. The quantity of nonmetallic inclusions formed upon deoxidation, the type of inclusions formed and the amount of deoxidizer recovered in the finished steel depend upon

- (a) The amount of iron oxide in the steel before deoxidation.
- (b) The equilibria between the deoxidizer and the FeO in the steel.
- (c) The rate of diffusion of iron oxide from slag to metal.

"Provided no iron oxide is combined with other slag components in such a manner that its solubility in the metal is effected, the dissolved oxygen will be proportional to the relative slag oxidation. The solubility of oxygen at the melting point under an iron oxide slag approaches 0.21 per cent O or 0.95 per cent FeO.

"With components other than iron oxide in the slag, the amount of FeO in the steel will not correspond to the true solubility. Furthermore a correction factor must be applied for the oxygen in the slag existing as Fe_2O_3 whose existence may be explained by either an equilibrium between slag and metal as indicated by the reaction:



or by the assumption that at the slag-gas surface FeO is oxidized to Fe_2O_3 which is reduced to FeO at the slag-metal surface. The increase of Fe_2O_3 for slags rendered inactive followed by a decrease with returned activity point to the second explanation as more probable. A conversion factor of

$$\frac{3\text{FeO}}{\text{Fe}_2\text{O}_3} = 1.35 \text{ was used throughout this investigation.}$$

"In applying physico-chemical laws to solutions, concentration is expressed in terms of molecules. The mol fraction

of a substance is obtained by dividing the molal concentration ($\frac{\text{Wt. \%}}{\text{Molecular Wt.}}$) by the sum of the molar concentrations of

all the components of the particular slag. While the concentration of iron oxide in the metal should be expressed as above, it is comparatively low in most cases and may be considered as weight per cent, which is correspondingly proportional.

"The distribution law of Nernst may be stated as follows: If a substance be dissolved in two immiscible liquids, it possesses a constant distribution coefficient at a given temperature when it exists as the same molecular species in both solvents. Where " C_1 " and " C_2 " represent the molal concentrations in the two phases, and "K" is the proportionally constant known as the distribution ratio,

$$\frac{C_1}{C_2} = K.$$

"For bath temperatures of 2925°F. this distribution ratio as averaged from empirical data is given as

$$\frac{\text{Mol Fraction FeO in Slag}}{\% \text{ FeO in Bath}} = 3.17$$

This correspondence of data shows that all the iron oxide in the lime-iron oxide slags studied is free to act on the metal and that any compounds formed between lime and the oxides of iron are dissociated in the molten state. Evidence of compound formation is found in the increase of Fe_2O_3 content of the slag as the lime increases.

"In applying the results on solubility to basic open-hearth operation, it will be necessary to make the assumption that all of the iron oxide in such slags is free to act on the metal. It is certain that the lime in the slag has no effect on the solubility of iron oxide in the metal, and since in basic open-hearth practice the lime is always in excess over that required to form $\text{CaO} \cdot \text{SiO}_2$, it is probable that silica has so small an effect upon solubility that it may be neglected here.

"The elimination of carbon depends on the presence of iron oxide in the metal bath. As fast as the oxide diffuses from slag to metal it reacts with the carbon and the rate of elimination is therefore just equal to that of diffusion. When the oxide concentration reaches the value which would be

predicted from the distribution ratio, no further diffusion will take place. At this point slag and metal are in equilibrium with respect to oxygen and the carbon in the bath is in equilibrium with dissolved FeO.

"There are no direct determinations of equilibrium in the metal phase on the reaction:



over the temperature range of open-hearth operation. When the equilibrium is reached, the concentrations of the reacting substances may be expressed (according to the law of mass action) by the equation:

$$K = \frac{1}{(C) (FeO)}$$

From the values of " K_e " shown in detail in the original publication, it becomes possible to calculate the relations of residual carbon and iron oxide for all possible variations of slag oxidation and temperature.

"The extreme importance of keeping the iron oxide content of the slag as close to that in equilibrium with the desired carbon is suggested. To do this it would be necessary to analyze working slags for FeO and control its concentration during the course of the heat which should be of distinct benefit in improving the quality of basic open-hearth steel, in reducing the number of heats rejected for improper analysis and in the more efficient use of deoxidizers and alloy additions."

In an unpublished private research on basic slags of lime-silica ratios between 2 and 4 to 1, Milton (10) then of the Johns Hopkins University faculty, suggested that "in contrast to acid slags, basic open-hearth slags crystallize completely on reasonably slow cooling such as was obtained by holding 40,000 pounds of the molten material undisturbed in a slag bowl for six days before sampling. The slags examined consist essentially of three compounds of which the first is always present and characteristic: the di-calcium silicate, the mixed divalent oxides and a compound of ferric iron related to the spinels, $RO.R_2O_3$.

"All of these compounds show more or less variation from heat to heat. Although the di-calcium silicate can vary little in chemical composition, its appearance depends on the conditions of crystallization, freedom from inclusions of other

substances and whether or not inversion has taken place from one crystalline modification to another. The divalent oxides can vary greatly in composition, being solid solutions: there is evidence of unmixing in both the liquid and solid states. While the separation of the actual compound from the slags proved unexpectedly difficult and the direct evidence of quantitative analysis is not yet at hand, all considerations point to $2\text{CaO}.\text{SiO}_2$ as being an essential component of these slags.

"In these particular basic open-hearth slags there is always an excess of basic oxides,— CaO , MgO , FeO and MnO , over the acidic oxides. These crystallize out in definite crystals of striking optical character especially when, owing to high CaO-MgO content, they are translucent. All these four oxides are to a greater or less extent mutually soluble: in these slags the oxide crystals vary in color by transmitted light from pale yellow to deep red to black.

"After separation of the oxide crystals from the matrix by treatment with a weak alcoholic solution of hydrofluoric acid, analysis of the residue indicates that all the FeO is in the free state in the samples examined, none in combination with SiO_2 , and that CaO and MnO are the oxides which combine with the minor acidic oxides, P_2O_5 , TiO_2 , Fe_2O_3 , rather than MgO and FeO .

"All of these slags contain trivalent oxides, mainly Fe_2O_3 , with some Al_2O_3 and Cr_2O_3 . Under certain conditions these oxides can exist in the free state but here form compounds with the divalent oxides of the general type $\text{RO}.\text{R}_2\text{O}_3$. The spinel compounds that may ordinarily be formed in a basic slag are magnetite, $\text{FeO}.\text{Fe}_2\text{O}_3$, and calcium ferrite, $\text{CaO}.\text{Fe}_2\text{O}_3$. A magnesium ferrite might be expected but although the mineral $\text{MgO}.\text{Fe}_2\text{O}_3$ exists in nature whereas the former is unknown, under open-hearth conditions the lime compound is formed rather than the magnesia.

"In two slags in the presence of high FeO (36 per cent) and very low silica, there was found a compound absent in the others, at least in observable quantity, which possessed the appearance of an iron-lime silicate approaching the composition, $3\text{CaO}.11\text{FeO}.7\text{SiO}_2$."

In concluding the review of previous findings it should be noted that a considerable proportion of each abstract has been transcribed

directly from the original paper with little other alteration than omission. The large and valuable quantity of research directed upon metallurgical slags may well serve as an index of the importance of their careful regulation to the industry.

HISTORICAL DATA: SLAG OXIDATION AND STEEL MAKING

Several years after the institution of detailed metallurgical observation in the hot metal divisions of one of the largest steel plants in the country, it became evident that continued improvement of the steel quality for both rimmed and killed practices would require either phenomenally uniform blast furnace operation or a more exact and intimate knowledge of the effects of hot metal fluctuations in silicon, phosphorus, manganese and sulphur upon the actual steel making processes in the open-hearth. It was almost too much to expect blast furnaces subjected to the usual chemical variations of raw materials to maintain silicon analyses within 0.25 per cent ranges and yet there could be no question that the open-hearth suffered from numerous difficulties whenever the silicon content of the hot metal charge deviated from 1.15 per cent to any appreciable extent.

It must have been frequent and normal experience in every open-hearth shop that the ill effects of hot metal cycles are not only progressive and cumulative, but that the constant readjustment of melting and refining practices militates against any sort of standardization and seriously undermines the morale of the organization. Bath temperatures vary from the extremes of badly skulled ladles to excessively hot pouring with all the attendant troubles making for imperfect pit practice. In driving for temperature with low silicon iron, refractories and bottoms suffer; with the upswing of the blast furnaces, previously undissolved limestone is attacked by steel and slag and again bottom delays mount. Operating nuisances add to the difficulty of maintaining chemical specifications and off-grade heats increase; deoxidation practices are found to be inadequate; as the rimmed steel improves, more killed steel is rejected; a few days later the situation may be reversed; and always production rates fall with yields all along the line. The situation is not a happy one.

Not the least serious phase of the predicament lies in what might be translated as 'the delegation of responsibility' which the long-suffering mill man refers to the open-hearth superintendent who then condemns the iron in no uncertain or respectable language, while the blast furnace operator speaks in uncomplimentary fashion of raw

materials and, before the proposition has had time for presentation to whom ever may be held accountable for the original chemical and physical condition of the ore deposits, the situation changes in another direction, usually not helpful. As a protection, melting is slowed down or rushed according to conditions and alloys are wasted in deoxidizing the killed steel beyond the danger point. There is no protection for churned steel; either it rims or the consumption of home scrap goes up with discouraging persistence.

Table II
Effect of Hot Metal Silicon Upon .20 Per Cent C Max. Killed Billets
(Commercial Grade)

Silicon Range Per Cent	No. Heats	Steel Rejections	
		Pipe Per Cent	Seams-Scabs Per Cent
Below .90	38	2.1	12.3
Above .90	51	2.1	7.9

Table III
Effect of Irregular Bath Temperature Caused by Low Silicon Hot Metal Upon
.10 Per Cent C Max. Rimmed Sheet Bar

Tapping Temp.*	No. Heats	Dec. 1928	Jan. 1928	Oct. 1929
		Steel Rejections Per Cent	Steel Rejections Per Cent	Steel Rejections Per Cent
Above 2900 Degrees Fahr.	64	4.3	78	156
Cold Heats (2860 Degrees Fahr. Max.)	29	14.7	39	5

*Calibration of optical pyrometers described in detail in "Open-Hearth Temperature Control," Earnshaw Cook, A.S.M. 1935.

Having exhausted the more obvious metallurgical possibilities together with the patience of the blast furnace department in an effort to maintain consistent practices, it was decided to investigate carefully the influence of hot metal upon open-hearth slags and to discover, if possible, the resulting effects of physico-chemical changes of the slags upon practical steel making. The routine analysis of open-hearth slags was inaugurated in September of 1929 and has survived with beneficial and fascinating results on through the succeeding interval down to the present.

During several earlier years, continuous efforts had been made to establish by direct determination the equilibria known to exist between residual carbon, the oxides of the slag and such of them as existed in similar or reduced form in the steel bath. With certain refinements, the iron iodide method for residual oxides was developed to a point where consistent analyses checking within the normal

laboratory accuracy of 0.02 per cent could be obtained for uniform samples. Favorable agreement was found with duplicate samples analyzed by the Bureau of Standards using the hydrogen reduction method:

Table IV

Sample No.	Method	C	Mn	Si	Total Oxides	SiO ₂	FeO	MnO	Cr ₂ O ₃	Al ₂ O ₃	Total Oxygen Per Cent
"S-15"	Bureau of Standards	0.064
S-15	Iron Iodide Method	0.021	0.018	0.018	0.285	0.003	0.251	0.020	0.008	Tr.	0.067

Upon further investigation, however, it was found extremely difficult to obtain representative and necessarily unkilld bath samples. Continued reactions in the test mold gave low results and the formation of oxidized blow holes sometimes caused irregularities on the high side. After numerous failures with copper, iron and refractory molds; water quenching direct and in the test spoon; quenching in melted paraffin and in fused sodium chloride;—it was decided that the most comparable, if not necessarily correct results, were achieved by averaging iodine determinations on 10-gram chunks cut from the usual duplicate floor tests for similar series of heats representing the various conditions of carbon and slag oxidation as tapped at an average temperature of 2925 degrees Fahr. It was, however, essential to drill out all large blow hole cavities to reduce contamination. Duplicate samples failing to check were discarded entirely.

Previous conclusions from the literature regarding the total effective slag oxidation as that corrected for Fe₂O₃ seemed to have been corroborated (as also shown later in the discussion) and, since the variation of the per cent of equivalent ferrous oxide was directly proportional to that of its molecular fraction within the limits of experimental error (See Fig. 6)—it was possible to express the principal results of the research mathematically from the laws of mass action and distribution in percentage compositions as follows:

$$\text{FeO}_B = \frac{0.00033 \text{ FeO}_s}{C}$$

Where

FeO_B = per cent residual FeO in the bath.

FeO_s = per cent corrected FeO in the slag.

C = per cent residual carbon.

0.00033 = equilibrium constant for reactions at 2925 degrees Fahr.

As a check upon the original research and for the purpose of obtaining data concerning the effect of temperature upon the equilibrium constants, duplicate slag and steel, tapping and ladle tests were analyzed for a series of eleven low carbon, low manganese, rimmed contact rail heats. Since no addition other than a limited amount of aluminum was added to either furnace or ladle, it was anticipated that the temperature difference between tapping (2970 degrees Fahr.) and pouring (2810 degrees Fahr.) would offer the principal variation between bath and ladle tests. Averages of the significant determinations are as follows:

Table V										
Slag Analyses										
No. Heats 11		FeO _s 26.1		SiO ₂ 14.0		CaO 40.8		MnO 6.8		P ₂ O ₅ 1.8
										Fe ₂ O ₃ 10.1
Steel Analyses										
No. Heats	Test	Temperature Degrees Fahr.	C	Mn	P	Total Oxides	FeO	SiO ₂	MnO	K
11	B.R.	2970	0.052	0.119	0.198	0.155	0.007	0.029	0.00031
11	Ladle	2810	0.044	0.114	0.015	0.211	0.162	0.007	0.029	0.00027

While the results for K_{2810} were not as low as might be expected from the findings of other investigators, the values for "K" satisfactorily approached that of 0.00033 as reported for K_{2925} .

An approximation of the equilibria for residual iron oxides, in the same order of magnitude as reported in contemporary researches could then be estimated for 2925 degrees Fahr. as follows:

Table VI						
Residual FeO in Steel Bath						
Per Cent FeO _s	10 Per Cent	15 Per Cent	20 Per Cent	25 Per Cent	30 Per Cent	35 Per Cent
0.05 C	0.067	0.100	0.133	0.167	0.200	0.234
0.08	0.042	0.063	0.083	0.104	0.125	0.147
0.10	0.033	0.050	0.067	0.083	0.100	0.117
0.15	0.022	0.033	0.045	0.055	0.067	0.078
0.20	0.017	0.025	0.033	0.042	0.050	0.058
0.30	0.011	0.017	0.022	0.028	0.033	0.039
0.40	0.008	0.013	0.017	0.021	0.025	0.029
0.50	0.007	0.010	0.013	0.017	0.020	0.023

No illusions were entertained regarding the accuracy of this or other methods for the determination or calculation of incidental oxides residual in the steel.

Regardless of the absolute accuracy of quantitative analyses, the theoretical variations of residual iron oxide referred to carbon and the corrected slag oxidation appeared to have been approached for the carbon ranges below 0.10 per cent carbon, although actual de-

terminations with concentrations of carbon above 0.15 per cent were uniformly above the calculated figures for FeO_B . If then the relative oxidation of the bath can exert any important effect upon steel refining, its potentialities for a given carbon concentration may be best, if indirectly, examined by an intimate study of the oxidation and properties of melting furnace slags.

With the inauguration of routine slag analysis for the open-hearth, two important and associated laboratory problems developed immediately. In the past, determinations spasmodically requested by the operating department had been reported several days after receiving the samples with no thought of elapsed time. If the working of the heats was to be closely followed, FeO results must have been reported within at least thirty minutes after dispatching the furnace tests and before the conditions represented could become appreciably altered. It was further required that the necessary corrections for Fe_2O_3 , expressed as FeO, must be readily and promptly included in the report.

The direct calculation for two examples from composite daily slag averages most clearly explains the course finally adopted. It was assumed that the amount of FeO equivalent to a given quantity of Fe_2O_3 , could be calculated in the usual manner as follows:

$$\begin{aligned}\text{Fe}_2\text{O}_3 + \text{Fe} &= 3\text{FeO} \\ \frac{216}{160} (\text{Fe}_2\text{O}_3) &= 1.35 \text{ Fe}_2\text{O}_3\end{aligned}$$

To obtain a molecular balance the equivalent percentage of FeO in the slags must be equal to three times the mols of Fe_2O_3 multiplied by the molecular weight of FeO and corrected for the theoretically increased slag volume:

Table VII
Correction of FeO Determinations for Fe_2O_3

Example	No. 1 Per Cent	No. 2 Per Cent
Determined FeO	8.16	12.32
Fe as FeO	6.35	9.59
Determined Fe_2O_3	5.79	11.58
Fe as Fe_2O_3	4.05	8.15
Equivalent FeO (1.35 Fe_2O_3)	7.82	15.65
Sum FeO corrected	15.98	27.97
Sum FeO, Fe_2O_3	13.95	23.90
Volume Increment	2.03	4.07
Equivalent FeO(X).....	15.66	26.90
Total Fe(A).....	10.40	17.74
Expressed as FeO(B).....	13.36	22.80
X/A	1.505	1.515
X/B	1.172	1.179

Calculations for a long series of samples over a wide range of slag oxidations indicated that regardless of the Fe_2O_3 content, the total equivalent slag oxidation could be obtained with sufficient accuracy for ordinary purposes by multiplying a single total iron titration by an average factor of 1.51. This was one of the earliest indications of the balanced nature of basic open-hearth slags. (Fig. 6).

Having thus disposed of the slag correction problem, the time limit for returning reports from the laboratory was reduced to ten minutes (from the time received) by installing delivery tube systems and telautographs, speeding up manipulations, maintaining heated reagents, introducing hydrofluoric acid to accelerate solution of the samples and substituting a potassium bichromate titration incorporating the 1.51 correction factor with a diphenylamine indicator, to replace the slower outside indicator with potassium ferricyanide.

In the meantime, a rapidly increasing collection of slag determinations prompted the tabulation of a succession of heats with similar open-hearth charges arranged to show the possible influence of hot metal fluctuations upon the slag oxidation over a period when considerable difficulties were experienced with open-hearth temperatures, analyses and quality:

Table VIII
Slag Oxidation vs. Mixer Silicon

Date 1929	No. Heats	Avg. Silicon Mixer Per Cent	Slag Oxidation: FeO_3 Maximum Per Cent	Minimum Per Cent	Average Per Cent
Nov. 27	25	0.73	31	19	28
Dec. 2	26	0.82	29	15	23
Dec. 10	24	0.93	23	16	23
Dec. 15	27	1.28	21	15	21

Table IX
Hot Metal Silicon vs. Bath Temperature Low Carbon Heats

Average Silicon Per Cent	No. Heats	No. Skulled (2875 Degrees Fahr. Max.)	Per Cent Cold Heats
0.50/0.60	43	25	58
0.60/0.70	56	23	41
0.70/0.80	56	20	36
0.80/0.90	23	9	39
0.90/1.00	17	5	29
1.00/1.10	37	6	16

In addition to the well known temperature effects, it seemed that blast furnace chemistry could obtain an unmistakable modification of

slag oxidations which, other things being equal, subsequently appeared to be also a function of residual carbon:

Table X
Residual Carbon vs. Slag Oxidation

No. Heats	Carbon Per Cent	Average FeO _s Per Cent
98	0.05	27.3
268	0.06	26.6
660	0.07	25.6
634	0.08	24.6
473	0.09	24.1
307	0.10	23.8
181	0.11	22.4

Similar averages suggested that for a given tapping carbon, with uniform manganese in the charge, the manganese residual in the steel varied inversely with the slag oxidation:

Table XI
Residual Mn vs. Slag Oxidation

No. Heats	Average Carbon Per Cent	Residual Mn Per Cent	FeO Per Cent
305	0.08	0.09	29.0
706	0.08	0.12	27.5
860	0.08	0.15	25.5
885	0.08	0.18	24.0

The reversible migration of the element from slag to bath with increasing or decreasing FeO during the heat indicated this to be a result of slag oxidation as will be discussed hereafter in further detail.

Table XII
Daily Variations of Slag Oxidations

Heat No.	Carbon Per Cent	Manganese Per Cent	FeO Per Cent
69-488	0.08	0.14	16.4
62-463	0.09	0.18	17.2
60-443	0.09	0.18	18.2
59-455	0.06	0.21	19.1
60-444	0.07	0.14	19.4
58-489	0.09	0.15	19.8
66-510	0.09	0.20	20.1
61-485	0.08	0.18	20.1
59-454	0.08	0.18	20.5
68-464	0.08	0.15	21.0
58-490	0.07	0.20	21.8
62-464	0.08	0.14	22.7
69-489	0.07	0.19	23.0
63-425	0.08	0.11	23.7
65-511	0.07	0.14	23.7
61-486	0.07	0.13	24.4
58-488	0.07	0.16	24.5
59-453	0.07	0.17	25.6
64-523	0.07	0.12	26.1
65-510	0.07	0.15	32.2

While such departures from the mean slag oxidation may well have been suspected with differing end-points and fluctuating hot metal, the organization was not prepared for circumstances which occurred day after day with monotonous irregularity for apparently uniform charging. With corresponding preliminary carbons and hot metal of similar silicon content, the slag oxidations wandered from one extreme to the other with little or no consistency and without regard to furnaces, melters, or refining practices during any typical day's run as listed in Table XII.

The obvious question as to the possible influence of such remarkable deviations of slag oxidation within restricted time intervals upon the final analysis and quality of the steel was promptly answered in the history of two characteristic recarburized billet heats tapped almost simultaneously and shown below:

Table XIII
Open-Hearth Practice for High Carbon Billet Heats

Heat No.	C	Mn	Si	Stone Per Cent	Ore Per Cent	Hot Metal Per Cent	Si
Spec.	0.70	0.55	0.25
61-176	0.67	0.52	0.29	8.6	2.3	61.5	1.45
68-148	0.69	0.75	0.24	9.1	3.9	64.0	1.45

Heat No.	B.R. Tests			Temp. Tap	Alloy Add.			Mold Add.
	C	Mn	FeO		C	Mn	Si	
Spec.
61-176	0.06	0.11	28.0	2795	0.66	0.71	0.46	3 # Si
68-148	0.09	0.12	15.0	2780	0.63	0.73	0.34	None

With a difference of 13 per cent FeO in the slags and with comparable ladle additions, the heats possessed widely separated final analyses because of varying alloy efficiencies while "61-176" with higher FeO proved to be semi-killed and suffered serious surface rejections in billet form on the hot bed.

Table XIV
Steel Rejections for Heats of Table XIII

Heat No.	FeO Per Cent	Alloy Efficiency Mn Per Cent	Si Per Cent	Steel Rejections Per Cent	Remarks
61-176	28	58	63	11.0	Semi-Killed
68-148	15	86	71	4.3	O.K.

This problem of slag oxidation effects upon surface quality for steels produced to the same chemical specification was more conclusively emphasized by the statistical evidence furnished through the

records of chipping costs on 4" x 4" billets rolled from a full aluminum-silicon killed steel of the following specification:

Table XV

C			Mn			P			S			Si		
Per Cent			Per Cent			Per Cent			Per Cent			Per Cent		
0.10 Max.			0.35/0.45			0.025 Max.			0.025 Max.			0.05 Max.		
Chipping Costs Versus Slag Oxidation														
No. Heats	Prelim. Tests			Ladle Tests			Alloy Loss			Pipe Rejections Per Cent	Chip- ping Cost Per Ton			
	FeO Per Cent	C Per Cent	Mn Per Cent	C Per Cent	Mn Per Cent	Si Per Cent	Mn Per Cent	Si Per Cent	Al Per Cent					
7	17.3	0.06	0.16	0.10	0.43	0.057	0.12	0.05	0.107	11.9	\$1.06			
12	21.1	0.06	0.15	0.09	0.42	0.046	0.14	0.05	0.117	11.3	1.49			
12	25.4	0.06	0.12	0.09	0.39	0.042	0.17	0.05	0.128	8.8	1.90			

Granted clean pit practices and correct temperature control in furnace and ladle, the surface quality of silicon-bearing steels appears to be concerned with its relative freedom from light and heavy seams. The latter normally arise from ingot shrinkage cracks aggravated by higher alloy contents, particularly silicon, but which may be satisfactorily controlled by proper mold design, teeming speeds and temperature. The light or short seams are characteristic of insufficiently killed steel and result from small surface blow-holes or reaction spots. In pronounced cases of semi-killing, the ingots become red short, tear badly on the blooming mill and produce bars, slabs or billets with an appearance closely resembling burned steel.

Thus it may be noted in the preceding tabulation that despite greater aluminum additions, the heats with higher slag oxidation were definitely more susceptible to light seams in the ratio of their chipping costs. It was consequently concluded that the correct proportioning of deoxidizing additions with respect to the iron oxide content of the slags was essential both for maintaining chemical specifications and improving the quality of the product.

Interpretation of the manifest results of slag oxidation upon the production of churned steels for full-finished body sheets is clarified by a detailed review of the evidence relating to its manufacture. It is well known that steel which rims actively and occupies a minimum volume in the molds, indicative of relatively greater freedom from sub-surface blow holes, possesses the best internal and external characteristics as illustrated below. The rise or fall of the ingots referred to the original pouring height furnishes a satisfactory criterion for estimating the success or failure of the particular refining practices:

Table XVI
Character of Rimming Versus Rejections (.10 Per Cent C Max.)
(25 In. x 30 In. Untreated Molds)

Condition of Tops	No. Heats	Avg. Steel Rej. Per Cent	Remarks
Over 6 In. Rise	9	13.0	Semi-Killed
2 In.-6 In. Rise	39	7.2	Sluggish
Flat Rim	17	4.8	Active Rim
2 In.-4 In. Drop-Flat Rim	33	4.8	Active Rim
Over 6 In. Drop	12	15.8	Wild Heats

Semi-killed or over deoxidized heats rim sluggishly, rise from two to twelve inches in the molds and invariably make thin-skinned, shadowed ingots:

Table XVII
Volume Increment Versus Rejections (.10 Per Cent C Max.)

Estimated Rise	No. Heats	Avg. Steel Rej. Per Cent	Remarks
Up 0	11	2.4	Active Rim
Up 1 In.	68	2.9	Active Rim
Up 2 In.	61	3.3	Moderate Rim
Up 3 In.	15	5.0	Moderate Rim
Up 4 In.	2	9.1	Sluggish Rim
Up 5 In.	2	22.4	Semi-Killed

The tendency of improperly rimmed heats toward increased carbon segregation above the ladle tests is exemplified by the following tabulations of 0.10 per cent carbon sheet bar check analyses from the center location of the uppermost cut after 15 per cent top discard:

Table XVIII
Rimming Action Versus Carbon Segregation

Practice	No. Heats	Avg. Positive C Segregation Per Cent
Ingot Tops rising more than 2 In.....	20	.059
Ingot Tops rising less than 2 In.....	42	.039

The advantage of regulating the rimming action of steel in the ladle rather than by indiscriminate mold additions is suggested by the following summaries in which no heats with irregular temperatures or pit practices have been included:

Table XIX
Rimmed Heats With Ladle Versus Mold Control

	Date: January 1930		February 1930	
	No. Heats	Per Cent Rejected	No. Heats	Per Cent Rejected
Aluminum in Ladle only.....	95	5.2	102	3.4
Aluminum in Molds	27	13.3	14	10.2

It having been developed that neither wild, insufficiently deoxidized steel nor sluggish, semi-killed heats could be processed to the best advantage, the following studies were made in reference to slag oxidation:

Table XX
Mold Additions Versus FeO in Slag (.10 Per Cent C Max.)

Grade	No.	Good Heats	Wild Hts. Requiring Al Add.
		Avg. FeO Per Cent	Avg. FeO Per Cent
Rimmed Sheet Bar.....	49	21	4
Rimmed Skelp	77	20	20
			27
			24

Table XXI
Slag Oxidation Versus Shadowed or Semi-Killed Heats
(.10 Per Cent C Max. Rimmed)

Observation	No. Heats	Average FeO Per Cent
OK	50	23
Light Shadows	21	19
Medium Shadows	13	18
Heavy Shadows	3	18

The so-called "shadowed" ingots result from the proximity of primary blow holes to the surface of the steel, a condition characteristic of inactive rimming. This skin effect is more pronounced in the bottom half of the ingot and the consequently more rapid chilling of the periphery in proportion to the reduced thickness of the outer metallic layers at this location produces a temperature shadow easily recognized fifteen minutes after stripping.

It should be noted that the control of churned steel had been based upon standard aluminum additions to the ladle scheduled according to base charge, final carbon, tapping temperature and mold size. Since slag oxidations above and below the shop average of 20-22 per cent FeO produced wild or sluggish rimming action, respectively, it seemed obvious that the corrective additions should likewise be varied in relation to this effect. Such a schedule was evolved with quite satisfactory results as shown hereafter in the report.

In retrospect then, it may be concisely stated that the comparative oxidation of basic open-hearth slags may have a most important influence upon the chemical and physical properties of both rimmed and killed steels. The successful and profitable manufacture of ingots of either variety seems to require that the attention of the operating departments be persistently directed toward the physical chemistry of steel making as related to the most advantageous adjust-

ment of numerous conflicting variables in the accomplishment of temperature and deoxidation control.

THE PRACTICAL APPLICATION OF DEOXIDATION CONTROL

The practical application of deoxidation control again involves a separate discussion of rimmed and killed steels without regard to the intermediate species which, in the opinion of many able metallurgists, is a bastard product that may be depended upon to accomplish more concentrated grief than anything else with the doubtful exception of one special case,—capped Bessemer ingots.

It having been decided that the aluminum control of rimmed steel should be adapted to slag oxidations in addition to the practices previously outlined, the subsequent provisions were both brief and simple: an experimental schedule of aluminum additions was arbitrarily arranged by which sufficient deoxidizer was added to the ladle to combine with half the calculated residual iron oxide present in the steel under the particular conditions of carbon, temperature and slag oxidation. As the ratio of the combining weights of aluminum and ferrous oxide are four to one, the amount calculated was further divided by four and the formula became:

$$\text{Per Cent Al} = \frac{0.00033 (\text{Per Cent FeO}_s)}{(2) (4) (\text{Per Cent C})} = \frac{(0.00004) (\text{Per Cent FeO}_s)}{\text{Per Cent Carbon}}$$

While it was not possible to estimate the quantitative deoxidizing effects of the usual ferromanganese addition to the furnace, it was ventured that this would be sufficiently uniform, when varied of itself according to slag oxidations, to maintain a constant final manganese. This latter was readily calculated from average manganese yields based directly on known shop practices and is reproduced below together with the aluminum schedule:

Table XXII								
Alloy Yields: 80 Per Cent Ferro-Mn: 0.12 Per Cent C Max. Rimmed Steel								
Manganese In Per Cent of Base Charge*								
Furnace Addition: Time, 8 Minutes								
Per Cent Mn Addition	0.40	0.50	0.60	0.70	0.80	0.90	1.00	
% FeO _s Per Cent FeO _s								
0.067	12	0.18	0.22	0.26	0.31	0.35	0.40	0.44
	14	0.17	0.21	0.25	0.29	0.34	0.38	0.42
	16	0.16	0.20	0.25	0.28	0.33	0.37	0.41
	18	0.16	0.20	0.24	0.28	0.32	0.36	0.40
0.111	20	0.15	0.19	0.23	0.27	0.31	0.35	0.39
	22	0.15	0.18	0.22	0.25	0.29	0.33	0.37
	24	0.14	0.18	0.22	0.25	0.29	0.33	0.36
	26	0.14	0.17	0.21	0.24	0.28	0.31	0.35
	28	0.13	0.16	0.20	0.23	0.26	0.30	0.33
0.167	30	0.13	0.16	0.19	0.22	0.25	0.29	0.32

*The base charge equals the total metallic charge multiplied by the average furnace yield.

Table XXIII
Corrective Aluminum Ladle Additions—Rimmed Steel
(Aluminum in Per Cent of Base Charge)*

	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Final C	0.05	0.07	0.10	0.12	0.15
Final Mn	0.12	0.30	0.35	0.40	0.40
Per Cent FeO _s					
12	0.010	0.007	0.005	0.004	0.003
14	0.012	0.008	0.006	0.005	0.004
16	0.013	0.009	0.007	0.005	0.004
18	0.015	0.010	0.008	0.006	0.005
20	0.017	0.012	0.008	0.007	0.005
22	0.018	0.013	0.009	0.008	0.006
24	0.020	0.014	0.010	0.008	0.007
26	0.022	0.015	0.011	0.009	0.007
28	0.023	0.016	0.011	0.010	0.008
30	0.025	0.018	0.012	0.010	0.008

*The base charge equals the total metallic charge multiplied by the average furnace yield.

Inasmuch as the calculated aluminum addition of 0.013 per cent for 0.07 per cent carbon and 22 per cent slag oxidation happened to agree very closely with the empirical value previously standardized for average shop practices, it was decided to put the schedule into effect for further investigation. This program was finally modified to decrease slightly the aluminum factors and obtain more active rimming but always with the provision that such departures from the original base remained in proportion to the calculated variations of ferrous oxide* residual in the steel. Close adherence to the additions as scheduled for manganese and aluminum established a practice which obtained uniform rimming without mold additions for more than 80 per cent of the total heats subsequently processed under correct temperature control; i. e., tapped above 2925 degrees Fahr. and poured at 2700-2720 degrees Fahr. for 0.08-0.10 per cent carbon steel.

The action of the metal in the molds seems to be influenced by the condition of the bath after the ferromanganese addition and may best be controlled by effecting standard intervals from the time of addition to tapping as related to slag oxidation. It is particularly important to maintain uniform temperatures and final analyses closely conforming with those upon which the schedules have been based if the most satisfactory results are to be obtained. The use of carbometers for rapid preliminary carbon is invaluable in this respect.

During this several years critical investigation of churned steel making, the gradual and satisfactory amelioration of bar yields for full-finished sheets bears testimony to the general advantages to be derived from careful study of the more significant phases of the

*"Lack of confidence in the analytical and theoretical methods for estimating residual iron oxide should be emphasized. They offered a successful approach at the time and are reported as a matter of record."

process: hot metal quality; temperature and deoxidation control; and last, but equally important, pit, mold and mill practices:

Table XXIV
Rimmed Sheet Bar Yields

Date	Bar Yield
1926	54.6
1927	61.8
1928	68.6
1929	73.2
1930	74.5
1931	76.4
1932	77.8

As previously outlined, the successful manufacture of first or forging quality killed steels requires careful deoxidation beyond a safe minimum with proper temperature regulation in the open-hearth, followed by mold and mill practices designed correctly to handle a very susceptible and readily abused product. Where final inspection standards (as for structural steels) or the ultimate mechanical reduction of the material to small cross-sectional areas (as for certain types of rods and sheets) do not exact the freedom from light seams commanded by hot and cold upsetting stock, the original methods of partially deoxidizing the metal in the ladle and more completely in the molds were often able to maintain yields of semi-finished product approaching eighty-six per cent. As for rimmed steels, the continued reactions in the molds exerted suppressive effects upon piping while the lower silicon and alloy contents tended to decrease ingot cracks.

When, however, meticulous steel making received its greatest impetus from the demands of the munition, automotive and allied trades and the deplorable chipping hammer came into regular service, —the situation changed abruptly: seams, segregation, and questionable heat treating properties were prohibited to the lasting discredit and grief of the steel plant. The mills, unaccustomed to the drastically reduced yields occasioned by fully killed ingots, found no choice in the matter between enormous top discards or impossible reclamation costs as illustrated by the following typical example:

Table XXV
Chipping Costs of Low Carbon Killed Steel Versus Pipe Rejections

No. Heats	Top Discard	Pipe Rej.	B. R. Tests			Ladle Tests			Alloy Loss			Chip. Cost Per Ton
			FeO _s	C	Mn	C	Mn	Si	Mn	Si	Al	
6	15	1.6	24.1	0.06	0.11	0.09	0.35	0.04	0.19	0.05	0.12	\$3.11
11	15	9.6	22.2	0.06	0.13	0.09	0.39	0.04	0.18	0.05	0.12	1.07
14	15	15.3	20.7	0.06	0.16	0.10	0.45	0.05	0.11	0.05	0.12	0.86

It is generally conceded that the piping of ingots under comparable conditions is a direct function of relative killing and here above the importance of well-advised deoxidation practices is conclusively demonstrated. The usual experience of larger alloy losses accompanying high slag oxidation accomplished the anticipated result,—less pipe, but not less segregation, and ruinous chipping expense.

After deliberately balancing the mediums of deoxidation with slag oxidation, the desired improvement of surface quality at the expense of piping was immediately achieved as exemplified by the last three heats of the succeeding tabulation arranged by silicon contents:

Table XXVI
Chipping Costs of Killed Versus Semi-Killed Steels

No. Heats	Top Dis-card	Ladle Tests			B. R. Tests			Alloy Losses			Pipe Rej.	Chip. Costs
		Si	C	Mn	FeO	C	Mn	Mn	Si	Al		
					Per Cent							
4	15	0.03	0.10	0.36	25.0	0.07	0.13	0.18	0.06	0.11	4.8	\$3.00
9	15	0.04	0.09	0.41	22.0	0.06	0.14	0.18	0.05	0.12	10.7	1.50
15	15	0.05	0.09	0.41	21.8	0.06	0.14	0.14	0.05	0.12	11.6	1.32
3	15	0.08	0.10	0.47	17.3	0.07	0.17	0.08	0.03	0.12	13.7	0.88

It should be noted here that the large numbers of individual heat records required to obtain representative statistics are materially reduced by the minute exploration of supervised chipping and, as a rule,

Table XXVII
Calculated FeO_B vs. Equivalent FeO Deoxidation Loss

Alloy	Deoxidation Factor
Mn to MnO	: 1.0 (FeO_B)
Si to SiO_2	: 2.5 (FeO_B)
Al to Al_2O_3	: 4.0 (FeO_B)

Heats Recapitulated from Preceding Examples
(Unbalanced Deoxidation)

	B. R. Tests			Alloy Losses			Chip. Cost	Calc. FeO_B	FeO Equiv- alent Mn, Si Loss	FeO Equiv- alent Mn, Si, Al Loss
	C	Mn	FeO_B Per Cent	Mn	Si	Al			Per Cent	
1	0.07	0.17	17.3	0.08	0.03	0.117	\$0.88	0.082	0.155	0.635
2	0.06	0.16	17.3	0.12	0.05	0.107	1.06	0.095	0.245	0.673
3	0.06	0.16	20.7	0.11	0.05	0.119	0.86	0.115	0.235	0.711
4	0.06	0.14	21.8	0.14	0.05	0.119	1.32	0.120	0.265	0.745
5	0.06	0.15	21.1	0.14	0.05	0.117	1.49	0.117	0.265	0.733
6	0.06	0.14	22.0	0.13	0.05	0.122	1.50	0.123	0.305	0.785
7	0.06	0.13	22.2	0.13	0.05	0.118	1.07	0.124	0.305	0.777
8	0.06	0.13	25.0	0.19	0.05	0.120	3.00	0.138	0.330	0.770
9	0.06	0.11	24.1	0.19	0.05	0.120	3.11	0.134	0.330	0.810

combinations of reclamation expense from thirty or more heats furnish excellent criteria. Again the chipping costs and pipe rejections are proportional to the deoxidation. It may be further demonstrated (Table XXVII) that, while alloy losses are relative to the calculated residual ferrous oxide in this particular series of heats, the amounts of manganese, silicon and aluminum oxidized are far in excess of that theoretically required to combine with the FeO supposedly present in the bath.

Although it is possible that the residual iron oxide calculations are thus grossly in error, it seems more logical to believe that the excessive alloy losses are the result of continued slag equilibrium effects in replenishing the bath, conceivably enhanced by surface oxidation through atmospheric exposure during tapping, and by the frequently observed losses of silicon and manganese between the first and last ingots of the heats. It may also be suggested that large deoxidizing additions are necessary to furnish sufficient excess silicon or aluminum to insure completion of the reactions as the FeO concentration is progressively reduced toward zero.

The exact relationship between residual iron oxide and complete or semi-killing is somewhat obscure, particularly when the deoxidation required for higher carbon steels is considered. As indicated by the appearance of the ingot tops and rolling properties, a quite comparable state of deoxidation appears to exist for the following specifications:

Table XXVIII
Final Carbon vs. Necessary Alloy Additions

Grade	Prelim. Tests			Calc. FeO _B	Alloy Losses			Equiv. FeO	Ladle Tests		
	C	Mn	FeO _s		Mn	Si	Al		C	Mn	Si
Si Killed	0.06	0.16	20	0.110	0.14	0.12	0.44	0.10	0.42	0.12
Al-Si Kill	0.06	0.16	20	0.110	0.14	0.04	0.08	0.56	0.10	0.42	0.04
Si Killed*	0.20	0.20	20	0.033	0.20	0.20	0.65	0.84	0.70	0.22

*Recarburized in furnace.

The discrepancies between fact and theory are only too obvious where with 0.10 per cent carbon, 0.42 per cent manganese and 0.11 per cent FeO_B, the steel may be killed with 0.12 per cent silicon; while, with 0.84 per cent carbon, 0.70 per cent manganese and 0.03 per cent FeO, nearly twice as much silicon (0.22 per cent) is required to prevent bleeding ingots. For any given, narrow specification, the deoxidation effects seem to be closely proportional to the slag and

usually the bath oxidation. It has been frequently indicated that for all such chemical ranges, improved quality is associated with lower slag oxidations; but, while some sort of degassification or other unsuspected influence may have complicated conditions, it is at least certain that no simple fundamental solution of the problem has or can be advanced thus far.

Our limited knowledge of steel making slags in the basic open-hearth may then be summarized in three brief corollaries:

1. The manufacture of rimmed or killed steels of satisfactory quality requires the proper empirical adjustment of deoxidation practices to bath and slag oxidation for each particular chemical specification, with hot top control of piping where necessary.

2. Economies in furnace and alloy yields, the general physical and chemical properties of the ingots and uniformity of operation require the maintenance of a minimum slag oxidation consistent with phosphorus elimination.

3. The deoxidation of killed steel over a wide carbon range is not directly proportional to the residual iron oxide calculated by methods suggested herein or elsewhere.

THE DEVELOPMENT OF SLAG CONTROL

With the knowledge of the extreme irregularities of open-hearth slags during even daily periods (Table XII) the demonstrated necessity for controlled and balanced oxidation, together with certain operating economies possible of accomplishment—the advantages of predicting and controlling slag oxidations became immediately apparent. It could be shown for example that while the iron oxide increased proportionally with decreasing carbon, it was entirely probable that steel tapped at corresponding end points might well have slags of 14 per cent or 40 per cent FeO content:

Table XXIX
Extremes of Slag Oxidation With Low Residual Carbon

Heat No.	B. R. Tests		FeO _s
	Carbon	Manganese Per Cent	
71-305	0.05	0.10	40.5
65-321	0.06	0.12	17.3
61-265	0.05	0.15	16.9
72-285	0.05	0.07	38.1

The reduction of iron oxides thus involved two fundamental propositions: first, a general decrease of average shop analyses by modifications of the burden; and secondly, the controlled increase or decrease of iron oxide for individual heats which fell outside the prescribed limits. Routine heat analyses had indicated that rephosphorization above 0.020 per cent was probable when the slag oxidation decreased below 16 per cent in the presence of 2 per cent P_2O_5 . A compromised range between 16 per cent and 18 per cent FeO was therefore considered desirable.

From Campbell's text (1) as also from plant experiences with hot metal fluctuations, it was evident that under otherwise similar conditions, lower slag oxidations were associated with the relative silicon contents of the burden and the refining slags. Pursuing this line of thought, the earlier of slag control experiments included heats charged with high silicon Bessemer iron of which the following is a typical example:

Table XXX
Heat Charged With High Silicon Iron

Test No.	Hot Metal: 54 Per Cent				Si: 1.88	Mn: 0.30	P: 0.064	S: 0.034		
	Time	C	Mn	P	FeO	SiO ₂	CaO	MnO	P ₂ O ₅	Remarks
1	8:45A	1.16	0.04	0.027	17.2	30.9	31.4	5.4	1.3	Foaming
2	9:25	1.05	0.12	0.071	10.7	31.1	34.2	...	1.0	Lime Boil
3	10:05	0.91	0.12	0.049	10.7	30.2	35.0	7.0	1.1	Ore—4000 #
4	10:30	0.71	...	0.016	14.8	28.1	35.1	...	1.3	Ore—4000 #
5	11:20	0.46	0.10	0.019	16.4	
6	11:45	0.18	...	0.010	18.8	Ore—2000 #
7	12:20	0.13	0.11	...	14.7	23.9	37.6	5.4	1.1	
Tap	12:45	0.06	0.10	0.015	16.6	

There seemed to be no doubt that charging high silicon iron would accomplish 18 per cent maximum slag oxidations, but since the open-hearth gentlemen offered the conventional professional objections regarding banks, bottoms and time of heat, and impractical burdening was required for the blast furnaces, the proposition was dismissed with a recommendation for furnishing basic iron of 1.25-1.50 per cent silicon content,—one which remains entirely tenable in the particular plant under observation.

The investigation continued with what was hoped might prove a simple solution of the whole problem,—the use of manganese ore for charging and feeding, and of the following analysis:

	Per Cent
MnO ₂	83.80
SiO ₂	7.73
Fe	0.81
P	0.18

The heats normally melted at 15 per cent FeO and 0.60 per cent carbon; manganese ore contained negligible iron oxide; therefore, its addition to the furnace would reduce the carbon as required without, perhaps, increasing the slag oxidation. The effect of the addition of two tons of 84 per cent manganese ore to heat "60-044" is shown below:

Table XXXI
Effect of Mn Ore Additions

Time	C	Mn	FeO	MnO	Remarks
1:40	0.39	0.15	17.6	9.9
1:41	4500 # Mn Ore
2:05	0.28	0.20	20.2	14.2

An increment of 4 per cent MnO achieved reduction of carbon, accompanied however by increased iron oxide, and while the practice was quite unavailing for slag control purposes, the experiment was continued for a run on No. 61 furnace carrying only manganiferous ore of the following analysis:

	Per Cent
MnO ₂	18.3
Fe	52.2
SiO ₂	1.0

The results were as follows:

Table XXXII
Summary of Mn Ore Practice

Practice	Hot Metal Mn	Si	B. R. Tests C	Mn Per Cent	MnO	FeO	SiO ₂	CaO
Shop Average ...	1.70	0.89	0.07	0.16	7.9	25.2	14.6	40.1
No. 61 Furnace								
20 heats	1.69	0.94	0.07	0.17	8.4	28.0	12.4	39.7
11 heats	1.67	0.89	0.07	0.19	11.2	27.4	12.8	38.3
4 heats	1.61	0.86	0.08	0.20	14.2	26.9	13.1	36.4

Beyond slightly increasing the residual manganese, charging sufficient manganiferous ore to raise the slag concentration from 8 per cent to 14 per cent MnO, appeared to augment rather than improve the slag oxidations for No. 61 furnace as compared with shop averages for the corresponding period.

The preliminary investigations should not be dismissed without reference to a brief excursion into the realms of furnace atmospheres, of which two typical examples are deemed sufficient:

Table XXXIII
Effect of Furnace Atmosphere on Slag Oxidation

Test No.	Time	Heat 58-598			
		C	FeO _s Per Cent	Out-Going Gas CO ₂ O ₂	
1	2:34P	0.12	18.5	14.8	3.6 (Recarb.)
2	2:55	0.20	11.9	11.2	8.0
3	3:33	0.15	14.1	12.0	6.4
4	3:58	0.12	14.8	8.6	9.4
Heat 69-599					
1	12:45P	0.60	15.7	18.0	1.8
2	1:55	0.35	18.8	14.2	2.6
3	2:33	0.20	18.0	13.6	4.4
4	3:00	0.14	17.2	12.6	4.8

Although the relative state of oxidation of the atmosphere is undoubtedly an important factor in both the economical and metallurgical operation of the furnace, the indiscriminate association of highly oxidizing gases with opposing slag oxidations temporarily discouraged further investigation.

At this stage of the research a series of analyses, arranged by percentages of silica for comparable tapping carbons, re-directed attention to the lime-silica ratio of finishing slags:

Table XXXIV
Lime-Silica Ratio vs. Slag Oxidation

No. Hts.	Per Cent							
	C	Mn	FeO	SiO ₂	CaO	MnO	P2O ₅	CaO/SiO ₂
18	0.064	0.129	15.5	23.0	42.4	5.9	2.1	1.84
15	0.063	0.138	17.7	19.7	41.6	6.2	2.0	2.11
37	0.063	0.151	19.6	16.7	42.5	6.7	2.2	2.54
40	0.066	0.153	22.6	14.9	42.3	6.7	1.6	2.84
40	0.064	0.144	26.8	13.0	41.4	7.1	1.6	3.19
40	0.065	0.126	30.9	11.7	39.7	7.2	1.6	3.39
100	0.055	0.110	36.4	10.1	39.9	5.7	1.8	3.95

Here with normal burdening practices, under similar conditions of refining, the slag oxidation appeared to be almost a direct function of the lime-silica ratio as charted in Fig. 1.

Striking optical effects of the changing acid-basic oxide ratio may be observed by examination of petrographic sections of high and low silicate slags with transmitted light. According to Milton (10), the characteristic appearance shows dark grey crystals of miscellaneous free oxides; the rounded grains of the red brown FeO-MgO phase; the yellow brown MnO-CaO phase; the long black prismatic ferrite grains of the type RO.R₂O₃; and the white ground mass of di-calcium silicate. A distinctive feature of the slides is the gradual transition from a clear white and black, silicate-oxide pattern at the

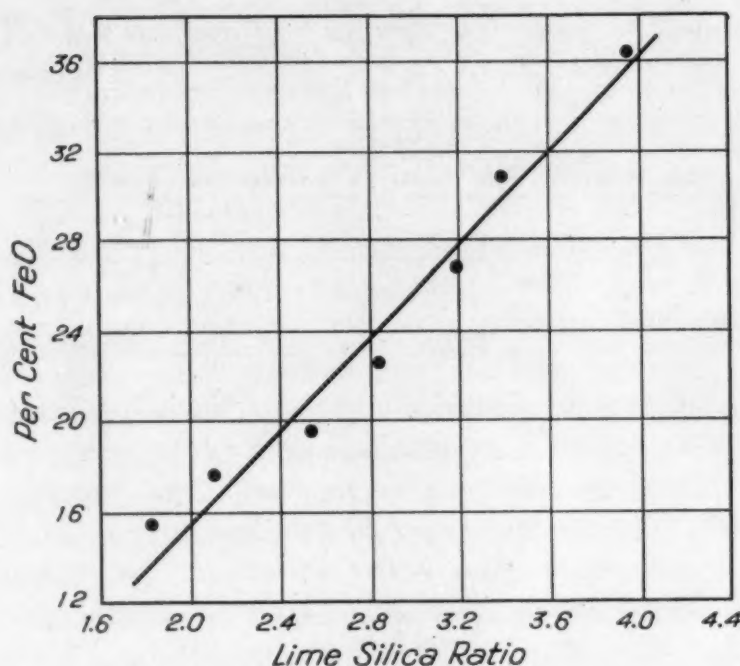


Fig. 1—Slag Oxidation Versus Lime-Silica Ratio for 0.07 Per Cent Carbon.

$2\text{RO} \cdot \text{SiO}_2$ composition with 22-25 per cent SiO_2 , to a brilliant, superimposed orange-red background as the $\text{RO} \cdot \text{Fe}_n\text{O}_n$ component appears in proportion to the decreasing silicate.

A logical, if unorthodox, curiosity advanced the notion that if the oxidation of sufficient silicon in the burden could, in the course of events regularly produce a finishing slag of low iron oxide content at 0.06 per cent carbon, the direct addition of silica to the charge or melt at the proper time might accomplish similar results with no dire consequences to the steel or furnace proper. Adequate and ample proof of the proposition was immediately available in a tabulation of twenty-five so-called "roof heats" collected happily over a protracted period. In explanation it might be added that if the silica brick roof of a unit in operation should collapse before the steel has or can be tapped, the melt is technically known, among other equally descriptive terms, as a roof heat. Whatever their ultimate destination or metallurgical utility, they are decidedly unpopular in or out of the furnace, —a not unnatural result of attempting to melt one hundred and fifty tons of solid metal covered with refractory debris under new, unseasoned bricks. It is too well known that such heats are usually tapped on the cold side, skull badly, are poured with outrageous pit practice and are often regrettably scrapped in whole or part by the blooming

mills. As might be suspected, they have an evil reputation, but most admirable slag control:

Table XXXV
Slag Oxidation: Roof Heats vs. Average Shop Practice

Practice	No. Hts.	C	Mn	FeO	SiO ₂ Per Cent	CaO	MnO	CaO/ SiO ₂
Roof Heats	25	0.08	0.14	16.9	20.4	43.3	5.9	2.12
Corresponding Avg. Shop Practice	600	0.08	0.14	22.4	16.1	42.9	6.2	2.66

With a silica content accidentally and artificially increased after melting, slag oxidations were obtained nearly 6 per cent lower than for the shop averages of the corresponding days' practices and it remained only to persuade the open-hearth department that corrective silicious additions might gain similar advantages for regular operation. Some days later the addition of river sand, analyzing 98 per cent SiO₂ to a basic open-hearth furnace was arranged for purposes of slag control.* Such a heat log is reproduced herewith accompanied by a contrasting example showing the opposite effect achieved by continued burned lime additions as the lime-silica ratio decreased by dilution:

Table XXXVI
Effect of Lime vs. Silica Additions Upon Slag Oxidation
Burned Lime Practice
Heat 59-184

Test No.	Time	C	Mn	P	FeO Per Cent	SiO ₂	MnO	CaO	Remarks
1	12:15P	0.69	0.24	0.025	12.5	20.7	...	41.9	8000 # Ore
2	1:00	0.27	0.16	0.012	20.9	17.4	...	43.7	3000 # Lime
3	1:25	0.17	0.13	0.012	21.7	16.8	...	42.5	3000 # Ore
4	1:45	0.11	0.16	0.010	22.8	14.9	...	45.1	3000 # Lime
Tap.	2:10	0.07	0.15	0.011	23.3	14.2	5.9	45.0	CaO/SiO ₂ = 3.18

Sand Practice
Heat 62-020

Test No.	Time	C	Mn	P	FeO Per Cent	SiO ₂	CaO	P ₂ O ₅	Remarks
1	10:45	1.39	0.14	0.086	8.6	4000 # Ore
2	12:10P	1.04	0.14	0.013	20.5	8000 # Ore
3	1:45	0.37	0.15	0.016	15.7	24.2	39.4	2.2	3000 # Sand (1:30)
4	2:10	0.16	0.15	0.025	13.9	2000 # Sand
Tap.	3:10	0.08	0.15	0.023	15.6	24.5	38.3	2.1	CaO/SiO ₂ = 1.57

It seemed almost a foregone conclusion, *other things being equal*, that maintaining a minimum practical lime-silica ratio by direct sili-

*U.S. Patent No. 2,046,811.

cious additions would accomplish the desired slag oxidation control, while, conversely, the ferrous oxide content could be builded up as required by the discriminate use of lime. The experimental data will be presented before discussing the mechanics of the procedure, but it is of interest to state at this point that the reduction of FeO from the slag by SiO₂ additions is unquestionably a chemical reaction between residual carbon and ferrous oxide which does not have the unsatisfactory chilling effect occasioned by late ore additions. The method is helpful rather than injurious to banks and bottoms.

Three other possible variations of control by regulating the lime-silica ratio suggested themselves in rapid succession: charging silicious material with the limestone, the substitution of Bessemer slag for river sand and variation of the percentage of fluxes charged with the changing amounts of silica available in the burden. Typical examples follow:

Table XXXVII
Effect of Charging Silicious Material Upon Slag Oxidation
Heat 67-005

Test No.	Time	Metallic Charge: 355000 #				Stone: 28000 #		Sand: 8000 #	Remarks
		C	Mn	P	FeO Per Cent	SiO ₂	CaO		
1	10:05A	2.54	0.07	0.053	10.8	11.4	
2	11:00	1.56	0.14	0.073	10.3	
3	12:00	1.24	0.29	0.080	9.3	12.6	
4	12:25	1.20	0.32	0.085	7.2	26.9	Melted
5	1:10	0.88	0.20	0.048	12.0	4000 # Ore
6	2:00	0.74	0.12	0.015	18.5	1500 # Lime
7	2:45	0.45	0.12	0.018	18.9	8000 # Ore
8	3:00	0.31	0.15	0.019	15.2	4000 # Ore
9	3:35	0.13	0.17	0.021	13.1	P ₂ O ₅ = 1.3 Per Cent
Tap.	4:29	0.06	0.14	0.018	15.5	19.3	37.0	7.9	CaO/SiO ₂ = 1.90

Providing the practice is not continued beyond a reasonable carbon content, it is here demonstrated that ore additions have little effect upon the slag oxidations; whereas, close melting heats deficient in SiO₂, reach maximum slag oxidations from atmospheric sources with no ore additions whatsoever, again confirming Campbell (1).

Table XXXVIII
Bessemer Slag Additions
Heat 60-236

Test No.	Time	Analysis: FeO 15 Per Cent, SiO ₂ 72 Per Cent, MnO 3 Per Cent							Remarks
		C	Mn	P	FeO Per Cent	SiO ₂	CaO	MnO	
1	9:55A	0.60	12.3	21.9	37.3	13.4	3500 # Slag 9:45
2	10:50	0.34	0.39	0.030	10.9	20.3	42.9	1500 # Lime
3	11:12	0.27	0.29	0.038	13.7	1000 # Slag
4	11:33	14.9	1500 # Ore
5	11:48	0.17	0.29	0.30	13.4	1000 # Slag
6	12:09	0.08	0.26	0.022	14.3	P ₂ O ₅ = 2.0 Per Cent
Tap.	12:20	0.06	0.24	0.020	15.4	18.5	43.4	10.1	CaO/SiO ₂ = 2.30

While it is effective in sufficient quantity, unless a profitable amount of iron and manganese is carried by the Bessemer slag to offset preparation costs, its bulk makes it less convenient for corrective additions to the furnace. It should be recognized that the utilization of Bessemer slag for purposes of deoxidation was originally employed and reported by F. O. Kichline at the Saucon Open-Hearth of the Bethlehem Steel Company in December, 1912.

If the silicious content of the open-hearth burden obtains a lime-silica ratio above 2.20 for usual American practices, quite considerable operating economies may be accomplished by reducing the stone charge to the minimum where rephosphorization becomes objectionable,—a condition arising when the slag oxidation decreases beyond 16 per cent in the presence of 2.0 per cent PO. The results of this procedure may best be illustrated by tabulation of average practices representing monthly periods of actual shop operations:

Table XXXIX
Effects of Stone Charge on Furnace Operation

<i>Materials Charged, Per Cent</i>	No. 66	No. 67	No. 69
Stone	8.6	8.5	5.0
Ore	3.8	3.5	3.8
Lime	0.3	0.3	1.1
Sand	0.4	0.4	0.3
Hot Metal	57.7	57.6	52.8
Cold Iron	0.2	0.2	0.2
Avg. Mixer Silicon	0.96	0.93	0.92
<i>BR Slag and Steel Analyses, Per Cent</i>			
Carbon	0.08	0.08	0.08
Manganese	0.19	0.19	0.19
FeO	21.1	21.1	19.7
SiO	16.7	16.2	18.0
CaO	40.5	41.7	39.4
<i>Practice</i>			
No. heats on checkers	138	130	316
Week of Campaign	10th	10th	23rd
Tonnage (5 weeks)	9530	9670	10600
Time Heats: Chg. to tap	10:18	10:48	10:10
Tons per hour	13.5	13.1	14.4
Gallons oil per ton	32.7	32.5	30.3
Per Cent Skulled heats	5.9	10.4	0.0
Furnace Yield	89.7	90.0	91.6
<i>Total Maintenance Delays</i>	39.55	21.25	17.23
<i>Bottom Time: Tap to Chg.</i>	:51	:58	:57
<i>Chg. Time: Start to Finish</i>	2:16	2:07	2:10

The average phosphorus and sulphur analyses as determined on ladle tests before and during the experimental run with 5 per cent stone charge are shown below:

No. Heats	Per Cent Stone	Per Cent Hot Metal	Avg. P	Avg. S
165	8-9	48-55	.017	.035
72	5	53	.022	.035

It is particularly interesting to observe that during the five weeks' operation listed above, No. 69 furnace, although twice the campaign age of No. 66 and No. 67 furnaces, enjoyed the following advantages with a decreased stone charge:

1. Production increased by 8.3 per cent for a total of 1000 tons.
2. Fuel consumption reduced by 7.7 per cent or an average of 2.3 gallons of oil per ton.
3. Furnace yield improved by 1.8 per cent.
4. No serious bottom delays.
5. No heats skulled above 3000 pounds and no failures for bottom pouring.
6. Slag oxidation reduced by 1.5 per cent.
7. Slag volume reduced by 20 per cent.
8. Decreased cost of fluxes despite unnecessary use of burned lime.
9. Favorably comparable hot bed yields as recorded, but not here reported in detail for entire run.

Before concluding the historical records of the research, a further limited investigation of the continuation of furnace reactions between slag and steel in the ladle may properly be recited. Samples representing the slag-metal surface in the ladle were obtained by teeming slag through the nozzle at the completion of pouring for the following series of high and low carbon killed heats:

Table XL
Slag Reactions in Ladle

No. Heats	B. R. Tests			Ladle Tests		FeO Loss
	C	Mn	FeO Per Cent	C	FeO	
25	0.06	0.15	21.0	0.09	19.0	2.0
25	0.15	0.19	24.0	0.68	15.0	9.0

While the entire analysis of the slags is not available, it may be accepted that the reduction of iron oxide in the ladle was the result of an increment of SiO_2 occasioned by oxidation of the usual ferro-silicon addition together with solution of silica from the ladle linings. Since the iron oxide losses for the higher carbon heats were four and one-half times those for the lower carbon steel, it seems highly probable that the materially increased reduction of FeO from the slags in the former case was the result of further chemical action induced by SiO_2 formation between slag and metal in the ladle in the presence

of available carbon in agreement with the unquestionable observation that the addition of silica to the furnace is entirely ineffectual in lowering the FeO concentration unless sufficient carbon is remaining in the bath to complete the reaction.

Where a final silicon of 0.10-0.12 per cent is usually capable of killing the softer steels up to 0.12 per cent carbon, it is necessary to specify a minimum of 0.20 per cent silicon to achieve the same results with heats above 0.30 per cent carbon. A reasonable deduction might attribute to the greater potential reaction speed of the higher carbon lime-silica equilibria, this seemingly contradictory effect requiring larger proportional deoxidation for steels of certainly lower residual iron oxide content. The slag-metal reaction appears to approach an end point in the furnace and assuredly slows down drastically for 0.06 per cent carbon baths at 14 per cent FeO, decreasing toward 10 per cent at 0.50 per cent carbon. Steel tapped at lower carbons should therefore require definitely diminished alloy additions in the ladle to perform comparable deoxidation because insufficient carbon is present to react with the FeO of the slag made available by the increased SiO_2 content resulting from the oxidation of ferrosilicon and solution of the refractories.

It seems likewise probable that the return of phosphorus to the steel frequently observed with higher carbon heats is a direct result of slag oxidation losses through the ladle reactions thus described. The reversion may usually be avoided by the addition of burned lime to the ladle before the slag commences to run from the furnace.

This concludes the general investigation of slag phenomena in the basic open-hearth under conditions of actual operation. While the citation of empirical data is necessarily limited, the findings are supported by additional detailed records of thousands of heats subsequently accumulated over a long period of years. The final section of this presentation will be devoted to an attempt at further interpretation of the more familiar slag-metal reactions according to the law of mass actions, together with the development of an accurate method for calculating finishing slag analyses from the raw materials of the furnace burden and the carbon of the bath at tapping.

PHYSICAL CHEMISTRY OF BASIC OPEN-HEARTH SLAGS FeO, CARBON EQUILIBRIUM

In any orderly arrangement of basic open-hearth slags at or near equilibrium with comparable residual carbons, their most significant

characteristic appears to be the complementary variation of equivalent iron oxide and silicon dioxide. Their relative oxidation under similar conditions of burdening may also be demonstrated to vary inversely with the lime-silica ratio as illustrated in Fig. 1. Theoretical explanation of what seems to be a well-established observation is the subject of four principal schools of thought:

1. The hypothesis of "automatic viscosity" proposed by Campbell and elaborated by Wilson, requires an increase or decrease of slag oxidation as the fluidity changes above or below the so-called "ideal condition." It has also been suggested that the more basic slags are more viscous and in them the oxygen from the furnace gases tends to build up at the slag-gas surface, increasing the FeO content. While the melting points and presumably the viscosity of the lime-silica system decrease with increasing silica, this is definitely not the case for the lime-silica-iron oxide system. Since the fusion points of normal basic slags vary inversely with the iron oxide content (Fig. 2) which decreases directly with increas-

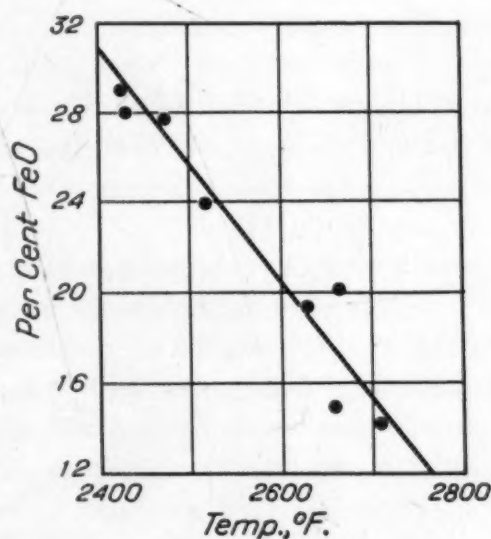


Fig. 2—Approximate Melting Temperatures of Open-Hearth Slags.

ing silica, the respective slag viscosities could be more logically considered a result rather than a controlling factor of FeO concentration. This proposition may be dismissed as a dogmatic interpretation of a more obscure, more reasonable chemical phenomenon.

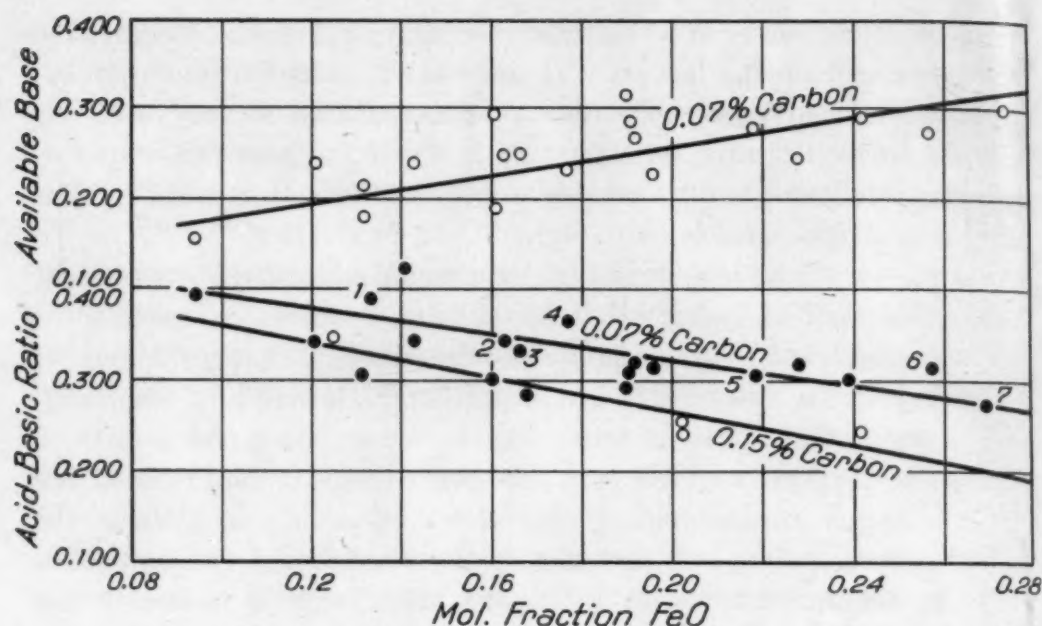


Fig. 3—Slag Oxidation Versus Basicity.

2. The possibility of an acid-basic oxygen balance was suggested by Fletcher in 1923, as promoted by an equalizing tendency toward a neutral condition.

3. The formation of inter-oxide compounds of the principal type $n \cdot RO \cdot P_2O_5$, $2RO \cdot SiO_2$ and $n \cdot RO \cdot R_2O_3$ was proposed by Stead and Colclough where the iron oxide may be present as $CaO \cdot Fe_nO_n$ and increases as free lime becomes available in greater amounts.

4. A fourth proposition appears in the possible occurrence of both ferrous and ferric oxides as weakly acid (proposed by Stead) in the presence of the strongly basic oxides of lime, magnesia and manganese with a mutual tendency to increase by atmospheric oxidation toward a neutral acid-basic molal balance in the absence of the stronger acidic oxides of silicon and phosphorus.

Since substances in solution react in proportion to their molecular fractions, testing of the tenable theories required the laborious calculation of a series of complete slag analysis according to the last three proposals under consideration as given in detail in the appendix. It follows that the mol fraction of equivalent iron oxide might then be proportional to: first, the acid-basic oxygen ratio; secondly, the mol fraction of available base; or, thirdly, to the acid-basic oxide ratio. Representative slags were selected from both

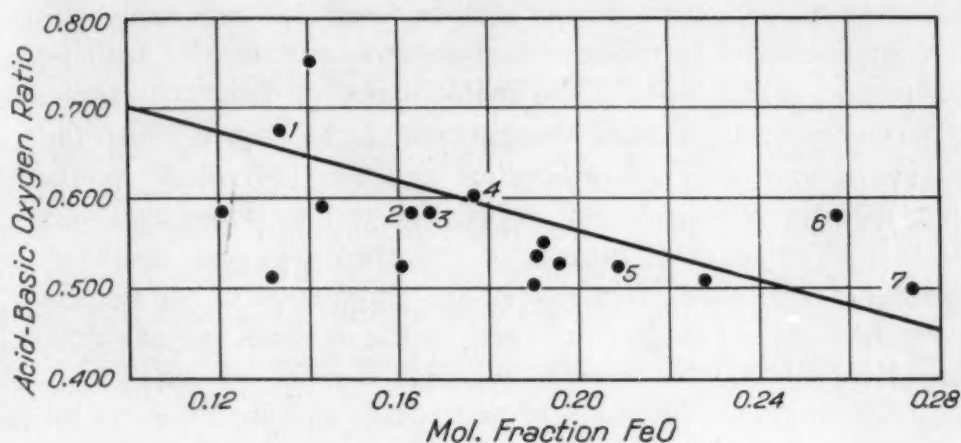


Fig. 4—Slag Oxidation Versus Basicity.

British and American practices in addition to those inherent in this investigation and were plotted accordingly against the iron oxide fraction as shown in Figs. 3 and 4.

Examination of these graphs at once eliminates the acid-basic oxygen corollary (Fig. 4) from the discussion since the out-lying points are both too numerous and too far from the average curve to allow a sufficient degree of probability or exactitude.

In this series of calculations the available base was obtained by subtracting the sum of twice the molds of SiO_2 ($2\text{RO} \cdot \text{SiO}_2$) and thrice the mols of P_2O_5 ($3\text{RO} \cdot \text{P}_2\text{O}_5$) from the molal sum of CaO , MgO and MnO comprising the usually recognized basic oxides present in the slags.

Petrographic analysis leaves little doubt as to the formation of $2\text{RO} \cdot \text{SiO}_2$ in the solid state with a critical minimum iron oxide content near a lime-silica ratio of 1.87 for certain American practices (Fig. 1) and the lime ferrate mineral hypothesis appears to be both sufficiently inclusive and satisfactorily convincing. (Fig. 3).

Computations of the acid-basic oxide ratio required that the molal sum of the percentages of SiO_2 , P_2O_5 , Cr_2O_3 , TiO_2 , V_2O_5 , Al_2O_3 be divided by the molal sum of the amounts of CaO , MgO and MnO present in the slag.

For the demonstrated comparable agreement on charts of identical scale (Fig. 3), the oxide fractions should therefore be equally capable of expressing the chemical habits of the general equilibria of the particular slag systems as well as permitting the development of less cumbersome equations. It may then be provisionally advanced that under uniformly oxidizing atmospheres of 2 per cent to 4 per

cent free oxygen, with similar temperatures and bath analyses, there is a regular trend for positive and negative variation of both ferrous and ferric oxides toward the maintenance of balanced equilibrium between the acid and basic constituents of the slag in which the iron oxides assume acid characteristics and the individual components enter into the relationships in proportion to their molecular fractions. Additional evidence in support of this theory of slag equilibria will be offered through a discussion of the elimination of phosphorus and manganese from the steel bath and by the methods for calculation of finishing slag analyses from the original furnace burden.

The equations for the acid-basic oxide equilibria may be written as shown below:

From Fig. 3

Residual Carbon	Equation	
0.07 Per Cent	M.F. FeO = $0.710 - 1.60 R$	(1)
0.15 Per Cent	M.F. FeO = $0.490 - 1.09 R$	(2)

Fig. 5, the most regular of all the data charts presents the locus of points for the percentage of equivalent iron oxide (FeO_s) against its actual molecular fraction for all conditions of carbon and acidity. This curve may be expressed mathematically as follows:

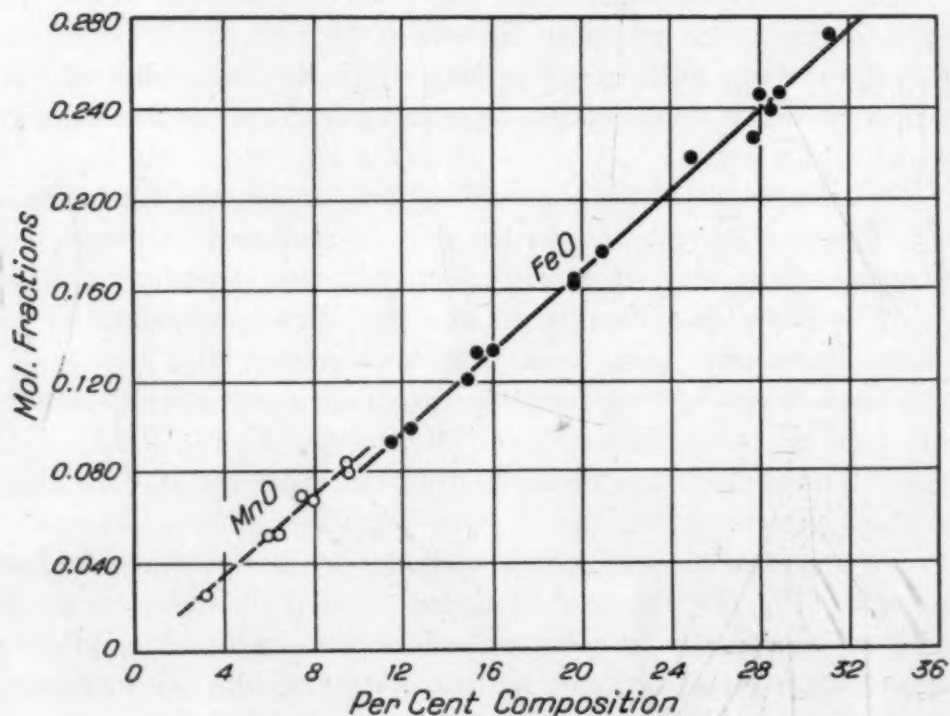


Fig. 5—Mol Fractions FeO and MnO Versus Per Cent Composition for 0.07 Per Cent Carbon.

$$\text{Per Cent FeO} = 111(\text{M.F. FeO}) + 1.2 \quad (3)$$

$$\text{Total Mols} = \frac{0.0139(\text{Per Cent FeO})}{\text{M.F. FeO}} \quad (4)$$

Considering the numerical variation of the total mols (4) for the slag series, this function of the iron oxide is remarkably consistent and is most important in its adaption to an extremely simple method for the calculation of slag weights and compositions from the furnace burden as subsequently presented. Proceeding to the

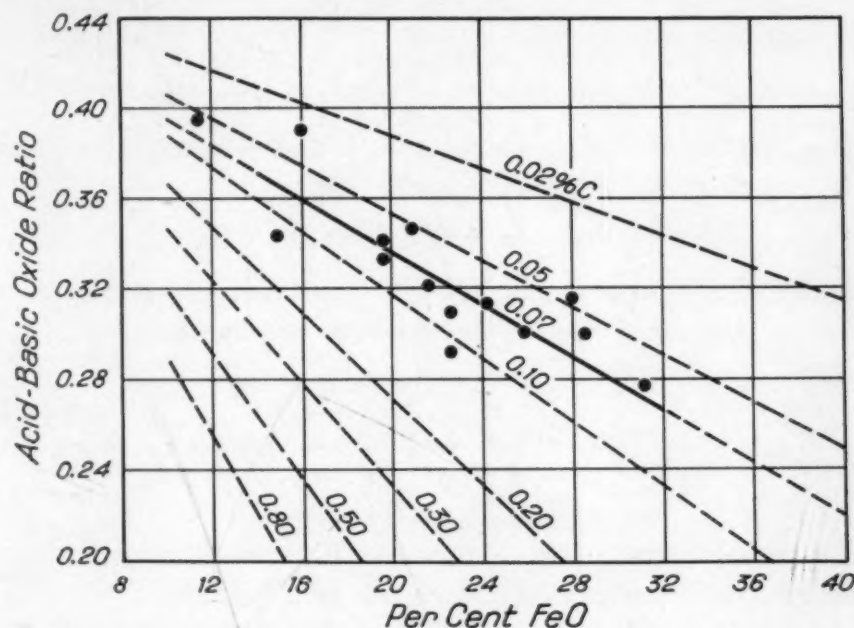


Fig. 6—Acid-Basic Oxide Ratio Versus Per Cent FeO.

acid-basic oxide ratio versus the per cent of equivalent iron oxide (Fig. 3), application of the straight line formula give the ensuing empirical equations (5) and (6) for 0.07 per cent and 0.15 per cent carbon. As a check on the results, it is interesting to observe that solution of the mol fraction equations for the same conditions closely agrees with that of the iron oxide equations although the two groups of data were independently charted in Fig. 3 and Fig. 6, respectively.

Solution of Equations (1), (2) and (3)		
Residual Carbon	Equation	
0.07 Per Cent	$\text{Per Cent FeO} = 80.0 - 177.6R$	(5)
0.15 Per Cent	$\text{Per Cent FeO} = 55.4 - 121.0R$	(6)

By substitution of values from equations (5), (6) and a special (32)* low carbon, high iron oxide electric furnace heat, the following working formulae are obtained:

* (appendix)

No.	Per Cent C	Log C	Per Cent FeO _s	Log FeO _s	R	Log R
1	0.025	-2.398	55.5	1.744	0.242	-1.384
2	0.07	-2.845	19.6	1.292	0.340	-1.532
3	0.07	-2.845	28.3	1.452	0.290	-1.462
4	0.07	-2.845	37.2	1.571	0.242	-1.384
5	0.15	-1.176	14.4	1.158	0.340	-1.532
6	0.15	-1.176	26.1	1.417	0.242	-1.384

The equation for the FeO_s — C equilibrium may have the general form:

$$(C^x) (\text{Per Cent FeO}) = K$$

Therefore:

$$(C^x)^a (\text{Per Cent FeO}_s)^a = (C^x)^b (\text{Per Cent FeO}_s)^b$$

By substitution (with R = 0.242) and solving logarithmically for "x" and "K", the equation may be written:

$$(C^{0.422}) (\text{Per Cent FeO}_s) = 11.73 = K_{(R\ 0.242)} \quad (7)$$

By solving equation (7) for "K" and variations of "R" with constant carbon the following values may be calculated:

No.	Per Cent C	R	Log R	Per Cent FeO _s	Log FeO _s	K	Log K
1	0.07	0.242	-1.382	37.2	1.571	11.73	1.069
2	0.07	0.290	-1.462	28.3	1.452	9.23	0.965
3	0.07	0.340	-1.532	19.6	1.292	6.38	0.805

It is evident from Fig. 6 that the FeO_s — R relationship with constant carbon is a straight line of the general form:

$$\frac{x - x_1}{x_1 - x_2} = \frac{y - y_1}{y_1 - y_2}$$

By substitution from the data for 0.07 per cent C:

$$K = 24.56 - 53.5R \quad (8)$$

The variable expression for "K" in terms of "R" may now be substituted in equation (7) and the general expression for the C — FeO_s — R equilibria tentatively described as:

$$(C^{0.422}) (\text{Per Cent FeO}_s) = 24.56 - 53.5R \quad (9)^*$$

For convenience in handling an otherwise awkward expression, the exponential term for carbon has been solved and illustrated in Fig. 7.

*Dr. Hugh S. Taylor has suggested that, if the various assumptions and data be correct, the several equilibria equations involving decimal exponents or those greater than the second degree may be conceived as representing the mean value of a series of complex reactions rather than the simplified equations described herein. This is exemplified by similar exponential values obtained for the solution of sulphur dioxide in copper when Nernst's distribution law is applied.

Per Cent C	$C^{0.422}$	Per Cent C	$C^{0.422}$
0.01	0.143	0.30	0.603
0.02	0.192	0.40	0.680
0.03	0.228	0.50	0.747
0.04	0.257	0.60	0.807
0.05	0.283	0.70	0.859
0.07	0.325	0.80	0.912
0.10	0.379	0.90	0.957
0.15	0.450	1.00	1.000
0.20	0.502		

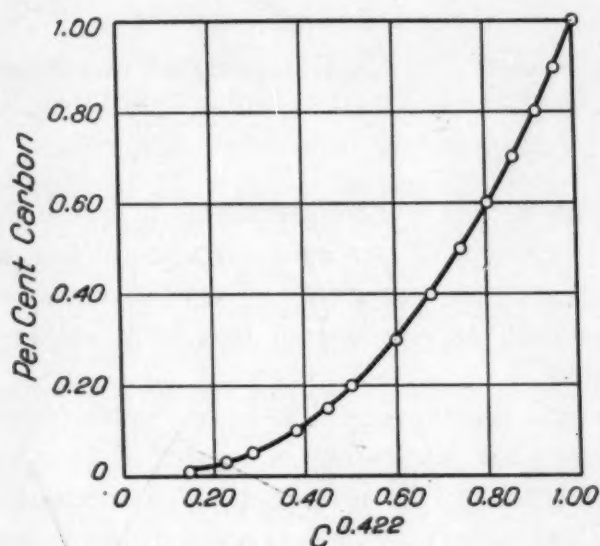


Fig. 7—Graphical Solution of $C^{0.422}$

The solution of equation (9) for different slag acidities is of interest and appears over the working range in Table XLI.

Table XLI
Solution of $C - FeO_s - R$ Equation (9) for Per Cent FeO_s
($R = \text{M. F. Acid Oxides} \div \text{M. F. Basic Oxides}$)

R Carbon	0.200	0.250	0.300	0.350	0.400
	Per Cent				
0.02	72.5	58.9	44.3	30.4	16.5
0.05	49.3	40.0	50.1	20.6	11.1
0.07	42.8	34.8	26.2	18.0	9.7
0.10	36.7	29.9	22.4	15.4	8.3
0.15	30.8	25.2	18.9	12.9	7.0
0.20	27.5	22.4	16.9	11.7	6.3
0.30	22.9	18.7	14.1	9.7	5.2
0.40	20.4	16.7	12.5	8.6	4.7
0.50	18.6	15.2	11.4	7.8	4.2
0.60	17.2	14.0	10.3	7.3	3.9
0.70	16.1	13.2	9.9	6.8	3.7
0.80	15.2	12.4	9.4	6.4	3.5
0.90	14.5	11.8	8.9	6.1	3.3
1.00	13.9	11.2	8.5	5.9	3.2

Recognizing that mathematical solution of empirical equilibria may not be carried too far beyond the experimental scope, equation

(9) is presented, nevertheless, as a possible summary of the resultant effects of acidity and carbon upon the slag oxidation subject to the end point limitations for a furnace atmosphere carrying from two to four per cent free oxygen. It is hoped that the method may offer a possible means of attack for the higher carbon reactions with subsequent correction of the constants over the useful range.

Regardless of the relative acidities, open-hearth slag oxidation seldom decreases below the following degrees:

Per Cent C	Approximate FeO _s End-Point, Per Cent
0.07	14.0
0.15	12.0
0.50/0.80	8.0

The slag calculations are comparatively accurate throughout the interval from 0.05 to 0.20 per cent carbon. While there is some evidence to indicate approximation of conditions above these concentrations, it should be emphasized that such values were mathematically obtained.

The slag-metal reactions of the basic electric furnace with reducing atmospheres are interesting in respect to very low iron oxide concentrations where, by the introduction of silicious material and carbon, the slag oxidation may be decreased to below 5 per cent FeO with, and only with, acid-basic oxide ratios in excess of 0.400 as predicted by the solution of equation (9). The reactions could not be expected to proceed beyond the point where the oxidation of the slag at the gas-slag surface proceeds as rapidly as the oxidation of the carbon at the slag-steel surface. Even with maximum practical acidity, the iron oxide content of the slag builds up with celerity if the melt is held in the open-hearth furnace at very low carbons for protracted periods of time.

This reduction of iron oxide from basic slags with increasing acidity seems necessarily to be the result of two probable, contributory factors: (1) simple dilution by the acid oxides, and (2) chemical reaction promoted by their presence. While a certain amount of dilution is unavoidable in the addition of sand to the furnace, the laboratory records of the following typical heat may clarify this point:

Heat No. 66-319									
Weight Slag: 47500 Pounds					Weight Steel: 310000 Pounds				
Time	C	Mn	FeO _s	FeO	Fe ₂ O ₃	SiO ₂	CaO	MnO	Addition
9:00 A.M.	0.19	0.13	15.7	12.0	4.2	20.2	47.5	4.5	—
9:01									4000 Pounds Sand (8.5 Per Cent)
9:30	0.10	0.12	12.5	10.1	2.7	29.1	43.1	4.5	—

By the addition of 4000 pounds of sand (8.5 per cent of the slag weight), the silica was increased from 20.2 to 29.1 per cent while the equivalent iron oxide dropped from 15.7 per cent at 0.19 per cent carbon, to 12.5 per cent at 0.10 per cent carbon. The losses of carbon and iron oxide are as follows:

	Carbon	FeO _s
Per Cent Loss	0.09	3.2
Weight Loss	280 Pounds	1510 Pounds

As the combining weights of FeO and carbon are proportionally 6 to 1, the actual carbon loss of 0.09 per cent checks closely with the calculated quantitative decrease of 250 pounds, or 0.08 per cent. Since also the straight dilution of the iron oxide from 15.7 to 12.5 per cent would have required an addition of 8500 pounds over and above the 4000 pounds of sand, there can be little doubt that this characteristic C-FeO-R equilibrium is the direct result of chemical action governed by the relative acidity of the slag and the oxidizing state of the furnace atmosphere. Further confirmation of this hypothesis exists in that the iron oxide reduction after silicious additions will not take place in the absence of carbon, that it may be increased without ore additions by means of burned lime, that the slag weights of high and low iron oxide heats are comparable for similar burdening, and that slag oxidations are entirely independent of the ore charged or added under conditions of normal practice.

Although considerable speculation has occupied investigators concerning the respective roles of ferrous and ferric oxides in the more important slag-metal reactions, no adequate decision has been reached thus far concerning the relative activities of FeO and Fe₂O₃. Based upon the increase of ferric oxide during periods of artificially retarded steel reactions after silicon additions to the bath, it has been suggested that oxidation of FeO to Fe₂O₃ occurs at the slag-gas surface followed by a reduction to FeO, which so enters into the more complex equilibrium, at the slag-metal surface. This premise is reasonably supported by the analyses from heat "66-319" whereby it is shown that both ferrous and ferric oxides are simultaneously reduced during periods of relatively retarded slag-gas reactions immediately after silicious additions.

Similarly, diagrammatic representation of the ferrous-ferric oxide relationship (Fig. 8) indicates a tendency toward the balanced equilibrium (observed by Fletcher in puddled iron slags) approximating

the molecular form, $3\text{FeO} \cdot \text{Fe}_2\text{O}_3$. It is also significant of this specific trend that analyses of slag oxidations corrected for Fe_2O_3 may be accurately calculated by means of a constant factor from the total iron titration. Excepting an unusual condition of dephosphorization dis-

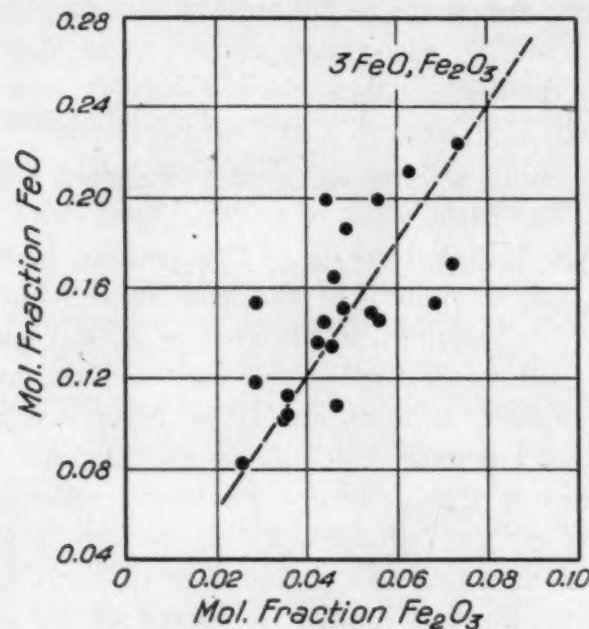


Fig. 8—Mol Fraction FeO Versus Mol Fraction Fe_2O_3 .

covered at one plant no irregular effects of Fe_2O_3 variations for slags of comparable corrected FeO_s analyses have appeared. The phenomenon has been studied indirectly by comparison of alloy yields under otherwise similar circumstances without positive results:

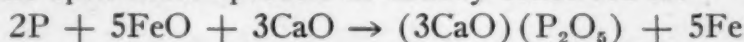
Table XLII												
Alloy Losses vs. Fe_2O_3												
High Carbon Rail Steel												
(C 80, Mn 65, Si 20)												
No. Hts.	BR		FeO_s	Fe_2O_3	Time Recarb. to Tap	Manganese			B. T. Si			
	C	Mn				Total	Ladle	Lost				
10	0.16	0.18	21.7	5.2	0:21	0.79	0.67	0.12	0.06			
10	0.17	0.18	21.7	10.5	0:20	0.77	0.62	0.15	0.05			
Low Carbon Killed Sheet Bar												
No. Hts.	BR		FeO_s	Fe_2O_3	SiO_2	CaO	MnO	P_2O_5	Alloy Loss			
	C	Mn							Mn	Si	P	Al
40	0.06	0.14	21.6	7.1	16.1	42.7	6.2	2.0	0.148	0.042	0.026	0.078
40	0.07	0.16	21.6	9.7	15.5	42.6	6.9	1.8	0.161	0.041	0.031	0.078

While imperceptibly higher alloy losses for heats of equal corrected FeO and higher Fe_2O_3 indicate a slightly increased degree of activity, the evidence discourages definite conclusions other than those

previously advanced that the slag-metal reactions are for all practical purposes appropriately associated with the resultant of the combined effects of the ferrous and ferric oxides. Further pragmatic confirmation of this assumption is available in the discussion of manganese and phosphorus distribution formulae subsequently presented.

Iron Oxide-Phosphorus Equilibrium

The form of chemical equation for the elimination of phosphorus in the basic open-hearth process as usually conceived is:



Where the components are expressed as mol fractions and the free lime replaced by the calculated available base above that necessary to combine with the acid oxides at $RO \cdot SiO_2$ and $3RO \cdot P_2O_5$, Herty has thus developed the equilibrium constant for the reaction from the law of mass actions:

$$K = \frac{(P_2O_5)}{(P)^2(FeO)^5(A \cdot B)^{0.5}} \quad (10)$$

and further states that the values cannot be depended upon above 4.0 per cent P_2O_5 .

While it may be shown that some sort of agreement with the experimental data up to 15 per cent P_2O_5 may be obtained by figuring the available base as the mol fraction of CaO , MnO and MgO above that required for combination as $3RO \cdot P_2O_5$ and the di-calcium silicate, $2RO \cdot SiO_2$, variation of individual cases from the average of these calculated equilibrium constants ($\log K = 5.270$) represent differences too great for acceptable experimental accuracy.

Rather than beginning with a precise chemical reaction, it is helpful to assume the general form of the equilibrium formula and solve a logarithmic expression of the applied law of mass actions for the exponents of the various functions which can then be incorporated as coefficients of the reacting molecules in the original equation which may be stated thus:

$$K = \frac{(P_2O_5)}{(P)^x(FeO)^y(A.B.)^z} \quad (11)$$

The available base being inversely proportional to the acid basic oxide ratio which has been demonstrated to be a function of the slag oxidation (FeO_s), this term appears unnecessary for solution and

the equation may be rewritten for direct substitution of experimental data as follows:

$$K = \frac{(P_2O_5^a)}{(P^a)^x(FeO^a)^y} = \frac{(P_2O_5^b)}{(P^b)^x(FeO^b)^y}$$

and

$$(P_2O_5^a) (P^b)^x(FeO^b)^y = (P_2O_5^b) (P^a)^x(FeO^a)^y \quad (12)$$

If the substitutions be made for heats of equal slag oxidations, FeO may be eliminated for the moment and the equation expressed logarithmically:

$$\begin{aligned} \log P_2O_5^a + x \log P^b &= \log P_2O_5^b + x \log P^a \\ x(\log P^b - \log P^a) &= \log P_2O_5^b - \log P_2O_5^a \\ x &= \frac{\log P_2O_5^b - \log P_2O_5^a}{\log P^b - \log P^a} \\ x &= 1.56, 1.62, 1.80, 2.01. \end{aligned} \quad (13)$$

Since data for heats of exactly the same slag oxidations with variable P_2O_5 were not available, it may be expected that the exponent of "P" approaches "2.00" which may be so employed in equation (12). It is of utmost importance that empirical substitutions be made from material representing the extremes of conditions if credible values are to be secured. To continue,

$$\begin{aligned} (FeO^b)^y(P^b)^x(P_2O_5^a) &= (FeO^a)^y(P^a)^x(P_2O_5^b) \\ y(\log FeO^b - \log FeO^a) &= 2(\log P^a - \log P^b) + (\log P_2O_5^b - \log P_2O_5^a) \\ y &= \frac{2(\log P^a - \log P^b) + (\log P_2O_5^b - \log P_2O_5^a)}{(\log FeO^b - \log FeO^a)} \\ y &= 3.01, 3.13, 3.32, 3.44. \end{aligned} \quad (14)$$

With the probable exponent of "FeO" determined as "3.00," the phosphorus equilibrium can be tentatively expressed as follows:

$$K = \frac{(P_2O_5)}{(P)^2(FeO)^3} \quad (15)^*$$

and the original chemical equation becomes:



The relative accuracy of this premise may be inferred by comparison with the calculated values of the constants for the different conceptions of the reaction

$$K = \frac{P_2O_5}{(P^2)(FeO)^3(A.B.)^{0.5}} \quad (\text{Herty}) \quad (10)$$

*See footnote page 374.

$$K = \frac{(P_2O_5)(R)}{(P)^2(FeO)^5}$$

(Above as modified
to this research)
(17)

$$K = \frac{P_2O_3}{(P)^2(FeO)^3}$$

(Proposed)
(18)

Although the oxide of phosphorus should have been calculated as P_2O_3 , rather than P_2O_5 , the results remain entirely comparable because the error in computing the mol fraction is exactly compensated by the discrepancy in reporting phosphorus as the pentoxide.

Table XLIII
Values of Log K_p for 2925 Degrees Fahr. and 0.07 Per Cent Carbon

Source	P_2O_5	Herty (#10) Per Cent	Modified (#17) Per Cent	Proposed (#18)
(11) Data	1.5	6.303	5.569	3.860
(14) Colclough	15.0	5.919	5.319	3.815
(15) Herty	5.8	5.816	5.362	3.847
(16) Stoughton	5.4	5.524	5.000	3.671
(17) Herty	2.1	5.352	4.747	3.713
(18) Herty	2.3	5.671	5.100	3.933
(20) Data	1.9	6.080	5.521	3.780
(21) Data	1.8	5.353	4.830	3.848
Maximum Difference	0.951	0.822	0.262
Log Average K_p	5.872	5.270	3.813

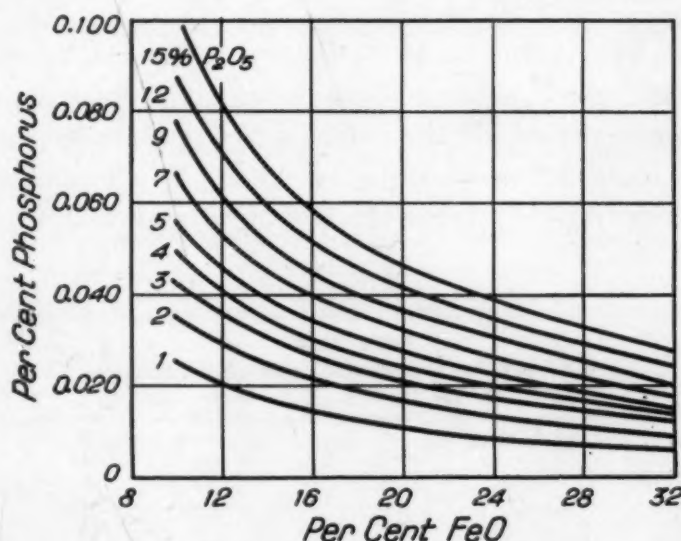


Fig. 9—P-FeO— P_2O_5 Equilibria.

The more satisfactorily consistent values for "log K_p " given by the proposed reaction (Equation #18) offers some evidence that, with sufficient basic oxides present to molecularly satisfy the more

important acid radicals, $2\text{RO} \cdot \text{SiO}_2$ and $3\text{RO} \cdot \text{P}_2\text{O}_3$, the chemical habits of lime and magnesia are at least properly described by the variations of iron oxide whether or not they may exert any fixation powers upon the phosphates. Inasmuch as the computations included only slag oxidations corrected for Fe_2O_3 in describing this equilibrium, additional corroboration of the total oxidation principle is also obtained.

It now becomes possible to calculate the variations of residual phosphorus which may be expected for all combinations of slag oxidation and phosphorus concentrations as exhibited graphically in Fig. 9 and numerically in Table XLIV.

Table XLIV
Variation of Residual P, P_2O_5 , FeO

Per Cent FeO	Per Cent P_2O_5								
	1	2	3	4	5	7	9	12	15
10	0.025	0.035	0.042	0.049	0.055	0.065	0.075	0.087	0.100
12	0.020	0.028	0.035	0.040	0.045	0.053	0.062	0.071	0.080
14	0.017	0.025	0.030	0.035	0.039	0.045	0.051	0.059	0.067
16	0.015	0.021	0.026	0.030	0.034	0.039	0.045	0.051	0.058
18	0.013	0.019	0.023	0.027	0.030	0.035	0.040	0.046	0.052
20	0.012	0.017	0.021	0.024	0.027	0.031	0.036	0.041	0.047
22	0.010	0.015	0.019	0.022	0.025	0.029	0.033	0.037	0.042
24	0.009	0.014	0.017	0.020	0.023	0.026	0.030	0.034	0.038
26	0.008	0.013	0.016	0.018	0.020	0.023	0.027	0.031	0.035
28	0.007	0.012	0.015	0.017	0.018	0.021	0.025	0.029	0.032
30	0.007	0.010	0.014	0.016	0.017	0.019	0.022	0.026	0.030
32	0.006	0.009	0.013	0.014	0.016	0.018	0.020	0.024	0.028

To further substantiate the P_2O_3 theory, a brief tabulation of the actual and calculated residual phosphorus for known conditions of operation is here arranged; the value of the phosphorus constant has been slightly increased to " $\text{Log } K_p = 3.830$ " by eliminating the lowest item (Table XLIII) from the averages, and so introducing the formula:

Table XLV
Determined vs. Calculated Residual Phosphorus
 $2\text{Log } P = \text{Log } \text{P}_2\text{O}_5 - 3\text{Log } \text{FeO} - 3.830$

Source	FeO	P_2O_5		
		2.0	5.8	15.0
		Per Cent		
Data	22.0	0.015
Reported by Herty	16.2	0.036
Reported by Colclough	15.2	0.066
Calculated (2P:3FeO)	0.014	0.038	0.069
Calculated (2P:5FeO)	0.013	0.045	0.087

The reaction and its constants could be more accurately and satisfactorily studied by applying the suggested methods to representa-

tive practices for high phosphorus charges where small errors of analysis for the low concentration American slags would be less conducive to manual discrepancy. The most important practical phase of the work lies in predicting the average residual phosphorus which may be expected for varying percentages of iron and phosphorus oxides. Since the necessary equilibrium constants may be obtained for a particular range by any of the several methods included in the research, the theoretical propositions are submitted as a basis for further investigation rather than a categorical assertion of truth.

It should be remembered when consulting the various tables that, while the *mols* of P_2O_3 and P_2O_5 are identical under the conditions of this investigation, the reported *percentages* of P_2O_3 in the equations must be multiplied by 1.29 for comparison with P_2O_5 :

P	P_2O_3	Mols P_2O_3 Per Cent	P_2O_5	Mols P_2O_5
1.00	1.775	0.0161	2.290	0.0161

To avoid confusion all data has been converted to P_2O_5 throughout the presentation.

Again cognizance of the acid-basic oxide theory of slag oxidation is indirectly supported by the congruous omission of terms concerning basicity in the phosphorus equilibrium formula which in this case conversely demonstrates the validity of the reciprocal relationship between iron oxide concentration and the degree of slag acidity.

An interesting prospective of the behavior of phosphorus is revealed in a series of samples procured at half hour intervals from heat "58-342":

Table XLVI
Progressive Elimination of Phosphorus

No. Time	1 8:00	2 8:30	3 9:00	4 9:30 Per Cent	5 10:00	6 10:40	7 12:20
C	1.66	1.33	1.10	0.92	0.79	0.47	0.06
P	0.036	0.056	0.065	0.048	0.036	0.017	0.005
Calc. P.	0.030	0.045	0.050	0.033	0.034	0.010	0.008
FeO _s	13.9	9.2	8.7	10.2	11.1	26.7	28.5
SiO ₂	26.0	27.4	27.2	22.5	23.5	17.7	13.8
CaO	30.7	34.2	37.8	28.5	40.0	36.1	39.6
P ₂ O ₅	2.2	1.4	1.4	1.4	1.5	1.7	1.6
Mols Acids	0.5289	0.5464	0.5335	0.4626	0.4702	0.3653	0.2902
Mols Bases	0.9322	1.0057	1.0446	1.0284	1.0529	0.9291	0.9674
Ratio	0.568	0.543	0.511	0.450	0.446	0.393	0.300

While it might be deduced from the equilibrium equation proposed for basic practices, neither the carbon nor the degree of acid-

ity of themselves seem to exercise as pertinent an effect upon the phosphorus concentration of the steel as that imposed indirectly through their joint control of the iron oxide content of the slag. Discounting possible temperature and atmospheric effects upon the reaction constant, the moderate agreement of the determined and calculated residual phosphorus at all stages of the illustrated heat lead to a similar conjecture. Since the elimination of phosphorus is an exothermal reaction accelerated by lower temperatures, a decrease below the equilibrium concentration might have been expected in the early stages of the heat, but the oxidation of carbon has proceeded rapidly during even the period of rephosphorization (Tests Nos. 1, 2, 3), and it seems probable that the preferential carbon reaction induced by virtue of its proportionally higher concentration may have accomplished a sufficiently reducing condition to temporarily prevent the attainment of normal equilibrium. Here once more deductive reasoning cannot be categorically accepted but the force of the argument lends itself to the opinion that a close approximation of the residual phosphorus may be obtained under many conditions of melting and refining by the formula:

$$\frac{P^2}{2925^*} = \frac{P_2O_5}{6761 (FeO)^3}$$

Spontaneous rephosphorization of higher carbon killed steel in the ladle is presumably the result of a secondary slag reaction with silica from alloy additions and refractories, and may best be controlled by taking the proper precautions to prevent it as previously described.

Mn-MnO-FeO Equilibrium

That the simple replacement of iron and manganese is probable in basic steel refining, should not preclude examination of the logarithmic expression of the law of mass actions which is particularly useful in determining the relative influence of excess bases upon the reaction as originally proposed by Colclough.



$$K = \frac{(Mn)(FeO)}{MnO} \quad (20)$$

It having been suggested that the reduction of manganese under otherwise similar conditions is directly proportional to a function of the available base, the second equation may be written:

$$K = \frac{(\text{MnO})(\text{A.B.})^n}{(\text{Mn})(\text{FeO})} \quad (21)$$

Considering the acid base ratio inversely proportional to the available base:

$$K = \frac{(\text{MnO})}{(\text{Mn})^x(\text{FeO})^y(\text{R})^z}$$

$$\frac{(\text{MnO}^a)}{(\text{Mn}^a)^x(\text{FeO}^a)^y(\text{R}^a)^z} = \frac{(\text{MnO}^b)}{(\text{Mn}^b)^x(\text{FeO}^b)^y(\text{R}^b)^z}$$

$$(\text{MnO}^a)(\text{R}^b)^z(\text{Mn}^b)^x(\text{FeO}^b)^y = (\text{MnO}^b)(\text{R}^a)^z(\text{Mn}^a)^x(\text{FeO}^a)^y \quad (22)$$

If "FeO" and consequently "R" remain constant, these terms may be cancelled and:

$$(\text{MnO}^a)(\text{Mn}^b)^x = (\text{MnO}^b)(\text{Mn}^a)^x$$

whence,

$$x = \frac{\text{Log MnO}^b - \text{Log MnO}^a}{\text{Log Mn}^b - \text{Log Mn}^a}$$

By substitution:

$$x = 0.70, 1.09, 1.11, 1.15$$

Similarly, by assuming the acid-base ratio, "R" to be a direct function of the slag oxidation, the exponent of "FeO" may be shown to approach "1.00." Substitution of these values in equation (22) obtains the following solution for the "z" exponent of "R":

$$z = \frac{(\text{log MnO}^b + \text{log Mn}^a + \text{log FeO}^a) - (\text{log MnO}^a + \text{log Mn}^b + \text{log FeO}^b)}{\text{log R}^b - \text{log R}^a}$$

$$z = 0.29, 0.35, 0.74$$

$$z = 0.46 \text{ (average)} \quad (24)$$

The relative accuracy of the three manganese equilibrium formulae may then be tested as before by a consideration of the individual values of their respective coefficients for the available data:

$$K_{2925} = \frac{(\text{MnO}) (\text{A.B.})^{0.5}}{(\text{Mn}) (\text{FeO})} \quad (\text{Herty}) \quad (25)$$

$$K_{2925} = \frac{(\text{MnO})}{(\text{Mn}) (\text{FeO}) (\text{R})^{0.5}} \quad (\text{Modified}) \quad (26)$$

$$K_{2925} = \frac{\text{MnO}}{(\text{Mn}) (\text{FeO})} \quad (\text{Proposed}) \quad (20)$$

Calculated values for the manganese equilibrium constants are as follows:

Table XLVII
Values of Log K_{Mn} for 2925 Degrees Fahr. and 0.07 Per Cent Carbon

Source Datum No.	MnO	Herty* No. 25	Modified No. 26	Proposed No. 20
		Per Cent		
1 Data	6.3	0.072	0.651	0.447
7 Data	6.0	9.931	0.470	0.192
2 Data	7.3	0.015	0.549	0.316
11 Data	3.9	9.821	0.557	0.390
13 Data	6.9	0.156	0.700	0.463
14 Colclough	7.3	9.954	0.594	0.337
16 Stoughton	8.1	9.941	0.474	0.207
18 Herty	5.3	0.115	0.688	0.436
19 Data	5.4	0.069	0.673	0.471
6 Data	7.0	9.976	0.500	0.254
24 Colclough	7.5	0.323
26 Colclough	7.8	0.296
Maximum Difference	0.335	0.200	0.264
Log Average K_{Mn}	0.133	0.593	0.356

*Calculated for $2\text{RO} \cdot \text{SiO}_2$

Where the maximum differences of Log K for the series are so closely comparable, any of the three conceptions of the reaction may be utilized with almost equal advantage. For example, substitution of corresponding data representing the extremes of operation in equations (27) and (28) obtains very similar estimations for residual manganese:

Example	No. 1 Per Cent	No. 2 Per Cent
C	0.07	0.07
MnO	4	14
FeO	30	12
R	0.282
Calculated Mn, (28)	0.059	0.423
Calculated Mn, (27)	0.061	0.450

The value of $K = 2.27$ satisfactorily approaches that of "2.00" as determined by Karber at 2910 degrees Fahr.

It being preferable to utilize the most consistent and simplest formula, it again appears that the manganese equilibrium *for normal basic slags* can be expressed (as those for phosphorus) by assuming the slag oxidation to be the characteristic resultant for the principal actions of carbon and acidity:

$$\frac{(\text{MnO})}{(\text{Mn})(\text{FeO})} = K_{2925} = 2.27 \quad (27)$$

Referring to heat "58-342" indicates, however, that the available base formula is more nearly representative of conditions where excess acids are present above equilibrium requirements and that better general accuracy may be obtained with the equation:

$$\text{Mn} = \frac{\text{MnO}}{(3.86)(\text{FeO})(\text{R})^{0.5}} \quad (28)$$

The large differences between certain calculated and determined values may result from the low temperature acceleration of the exothermal reaction in the earlier stages of the heat.

Table XLVIII
Progressive Elimination of Manganese 58-542

Test No.	Time	R	C	FeO _s	MnO Per Cent	Mn	Calculated Mn	
							(28)	(27)
1	8:00	0.568	1.66	13.8	10.5	0.10	0.26	0.34
2	8:30	0.543	1.33	9.2	9.4	0.16	0.36	0.47
3	9:00	0.511	1.10	8.7	8.0	0.22	0.27	0.42
4	9:30	0.450	0.92	10.2	7.3	0.23	0.28	0.32
5	10:00	0.446	0.79	11.1	7.0	0.22	0.24	0.28
6	10:40	0.407	0.47	26.7	6.4	0.14	0.10	0.11
7	12:20	0.300	0.06	28.5	5.1	0.10	0.08	0.08

Other things being equal averages of representative heats likewise indicate that the residual carbon within the scope of the investigation exerts little direct effect upon the elimination of manganese:

No. Hts.	C	FeO	MnO Per Cent	Mn	Calc. Mn
25	0.06	16.8	8.2	0.19	0.22
25	0.20	16.3	8.3	0.24	0.23
25	0.06	26.3	8.1	0.15	0.14
25	0.19	26.0	7.7	0.17	0.13

The residual manganese may be estimated for the usual variations of slag analysis as shown in Table XLIX and Fig. 10. These tables are in regular service in several open-hearth shops where it

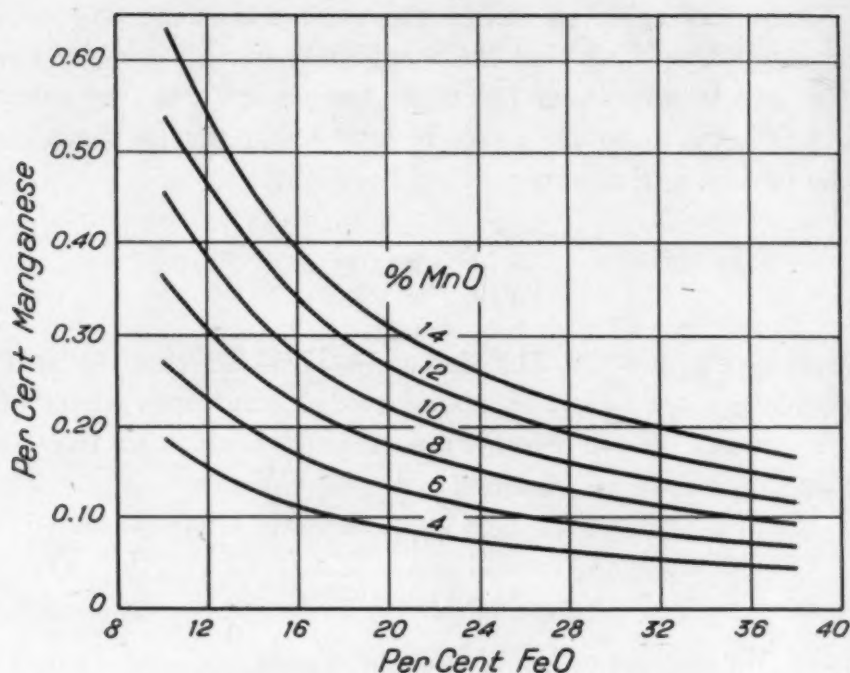


Fig. 10—Mn-FeO-MnO Equilibria.

has been found that closer estimations of the bath manganese may be obtained (for basing final additions of heats not killed in the furnace) by referring to the slag analysis of "FeO" and "MnO" than by depending on the direct determination of too early or non-representative steel tests.

Table XLIX
Variation of Residual Mn with MnO and FeO

MnO Per Cent FeO Per Cent	4	6	8	10	12	14
10	0.18	0.27	0.36	0.45	0.54	0.63
14	0.13	0.19	0.26	0.32	0.39	0.45
18	0.10	0.15	0.20	0.25	0.30	0.35
22	0.08	0.12	0.16	0.21	0.25	0.29
26	0.07	0.10	0.14	0.17	0.21	0.24
30	0.06	0.09	0.12	0.15	0.18	0.21
34	0.05	0.08	0.10	0.13	0.16	0.19
38	0.05	0.07	0.09	0.12	0.14	0.17

Elimination of Sulphur

The very low sulphur ores and fuel oils enjoyed by the plant where these studies were undertaken have together resulted in so low an average sulphur content for the steel at all stages of melting as to preclude any extensive investigation of the reactions affecting this vexatious element. We are indebted to Mr. William E. Steiner,

Chief Chemist of the Cambria Plant, for a brief examination of the behavior of sulphur in the basic open-hearth together with many other invaluable suggestions in the development and practical application of slag control.

As set forth in the earlier discussions of iron oxide equilibria where the principal differences in burdening occur in the variation of silicon and silica, the relative acidity of the slags is well expressed by the lime-silica ratio if, as usually the case, the concentrations of the remaining nonferrous oxides remain approximately constant. While the slag analyses are not sufficiently complete to permit direct calculation of the molal acid-basic oxide ratio, the measure of sulphur elimination in respect to the lime-silica ratio as reported by Mr. Steiner is pertinent and interesting:

Table L
Reversible Action of Sulphur

Heat No.	Decreasing Sulphur					SiO ₂	CaO	MnO	MgO
	C	Mn	S	CaO/SiO ₂	FeO Per Cent				
55-224	1.10	0.15	0.045	4.6	15.3	11.9	54.5	5.7
	0.22	0.09	0.037	4.6	29.7	9.2	53.0	7.6
48-553	0.36	0.16	0.035	3.1	19.9	15.8	49.5	7.5
	0.24	0.16	0.031	3.1	20.0	16.6	51.1	7.6
43-285	1.28	0.21	0.040	1.8	17.8	19.6	35.3	15.2
	0.30	0.28	0.033	2.7	17.6	15.6	41.5	13.8
49-268	0.35	0.18	0.042	2.3	15.9	18.3	41.9	11.2
	0.09	0.32	0.038	2.5	17.0	16.8	43.1	11.6
48-010	0.31	0.27	0.079	1.7	8.5	25.4	43.2	8.3	6.9
	0.07	0.17	0.063	2.1	13.3	19.0	40.2	7.6	13.9
	0.11	0.23	0.055	2.4	16.2	16.6	40.2	8.2	13.0
47-262	0.15	0.040	3.1	26.6	13.8	43.1	8.5
	0.08	0.14	0.029	3.9	22.2	13.7	49.9	7.2
	Increasing Sulphur					SiO ₂	CaO	MnO	MgO
	C	Mn	S	CaO/SiO ₂	FeO Per Cent				
48-543	0.40	0.22	0.041	2.9	16.2	15.6	45.5	6.6	11.8
	0.29	0.17	0.052	2.0	14.8	21.8	44.6	6.0	7.0
48-550	0.15	0.12	0.036	2.3	20.4	18.3	45.8	6.7	5.2
	0.07	0.14	0.040	2.1	15.7	22.3	47.2	5.6	4.6
47-264	0.67	0.15	0.050	3.2	18.3	15.7	50.6	5.2
	0.34	0.11	0.056	2.1	16.8	21.0	45.9	4.2
47-265	0.40	0.10	0.042	3.2	24.0	13.5	43.8	5.5
	0.27	0.13	0.041	2.1	18.3	20.9	44.7	5.4

It is quite evident from the summaries that sulphur concentrations can be slowly reduced in the basic open-hearth with a lime-silica ratio above 2.3:1 under normal conditions of operation. Further corroboration of these findings is introduced with average ladle analysis from the general data selected to represent the particular relationships:

No. Hts.	C	Mn	S	CaO/SiO ₂	FeO	SiO ₂	CaO	MnO
32	0.07	0.11	0.027	4.0	31.0	10.4	41.6	8.2
25	0.07	0.14	0.032	2.6	27.3	14.4	37.4	8.0
25	0.07	0.21	0.034	2.0	16.5	21.8	43.6	8.1

The coincidental occurrence of high percentages of lime with lower residual sulphur has been responsible for the frequent association of this very basic oxide with the sulphur removal which seems to be effective above the critical lime-silica ratio corresponding to slag oxidations of 20 per cent and acid-basic oxide ratios (R) of 0.300 to 0.340 in the carbon range from 0.15 to 0.07 per cent.

In retrospect it would appear that the tardy removal of sulphur in the open-hearth furnace by increased slag basicity at the sacrifice of time, furnace yields, slag oxidation and volume, lime additions and residual manganese is an expensive and hazardous undertaking. A knowledge of the most favorably desulphurizing conditions is assuredly valuable for emergency purposes but the concentration of this element should be properly controlled in the blast furnace where better and more economical regulation may be readily obtained. High sulphur, high phosphorus, low silicon hot metal is ruinous to open-hearth costs, quality and production, although comprehensive understanding and intelligent application of slag control can go far toward improving an otherwise impossible situation.

Slag Analyses and Burden Calculations

Acquaintance with the equilibrium constants for the more important bath reactions makes possible the calculation of the open-hearth burdens required to achieve definite specifications of slag oxidation, residual carbon, manganese and phosphorus or the final slag and steel analysis which may be expected from any particular combination of raw materials. It is interesting to consider briefly the influence of the more familiar and usual components of the slag upon the final chemical analysis of the melt. Reference to the various charts and tabulations requires that, for customary open-hearth practices and oxidizing atmospheres at least, the final iron oxide content of the slag should not be calculated below the end-points designated for the particular carbon. It may be assumed for example that slags possessing a sufficiently high acid-basic oxide ratio to obtain 10 per cent FeO_s at 0.07 per cent carbon will carry enough excess iron oxide to raise the concentration to the approximate end-point at 14 per cent FeO_s by dilution. (See data following Table XLI)

The equilibrium formulae required for burdening are as follows:

$$1. (C^{422})(\% \text{FeO}_s) = 2.456 - 5.35R \quad (9)$$

$$2. \text{M.F.} \text{FeO}_s = 0.009(\% \text{FeO}_s) - 0.108 \quad (\text{From } 3)$$

$$3. \text{ Total Mols} = \frac{0.0139 (\% \text{FeO}_s)}{\text{M.F.FeO}} \quad (4)$$

$$4. 2 \log P = \log \text{M.F.P}_2\text{O}_5 - 3 \log \text{M.F.FeO}_s - 3.830 \quad (\text{From 19})$$

$$5. \log \text{Mn} = \log \text{M.F.MnO} - (\log \text{M.F.FeO} + 0.5 \log R + 0.586) \quad (27)$$

$$6. \text{ Values for } C^{\text{res}} \text{ (Fig. 8)}$$

$$7. \text{ Slag Weight} = \frac{\text{Pounds Total Oxides Charged}}{100 - \% \text{FeO}_s}$$

A complete burden calculation for average practices with South American ores, 9 per cent stone charge and 4 per cent raw dolomite is shown below:

Table LI
Burden Calculations
Weight of Raw Materials Charged

	Lbs.	Mol Factor	Lb. Mols
Acids: 145 Ton Heat			
SiO ₂ (Metal, Ore, Fluxes).....	7500	1.67	12500
P ₂ O ₅ (Scrap, Metal)	1000	0.71	710
V ₂ O ₅ , TiO ₂ , Al ₂ O ₃ , Cr ₂ O ₃	2500	1.00*	2500
*Average			
Total Acids	15710
Bases:			
CaO (Stone, Dol., Lime).....	21000	1.79	37600
MnO (Metal, Scrap, Ore).....	3000	1.39	4170
MgO (Fluxes)	3000	2.50	7500
Total Bases	49270
Total Wt. of Oxides.....	38000

Acid Base Ratio, $R = 15710 \div 49270 = 0.319$

From Equation No. 1	Carbon	R	FeO	From Equation No. 7	Slag Wt. Lbs.
	0.07	0.319	23.2		49500
	0.10	0.319	20.8		48000
	0.15	0.319	16.8		45700

Estimated Slag Composition

Per Cent C	R	Slag Wt.	FeO	SiO ₂	CaO	MnO	MgO	P ₂ O ₅	Inc. Ox.
0.07	0.319	49500	23.2	15.1	42.4	6.1	6.1	2.0	5.1
0.10	0.319	48000	20.8	15.6	43.8	6.3	6.3	2.1	5.2
0.15	0.319	45700	16.8	16.4	46.0	6.6	6.6	2.2	5.5

Calculated Molal Composition
(Equations Nos. 19 and 27)

Per Cent C	Tot. Mols	Mols FeO	Mols MnO	Mols P ₂ O ₅	Mol Fraction		
					FeO	MnO	P ₂ O ₅
0.07	1.6200	0.3225	0.0849	0.0142	0.1990	0.0525	0.0088
0.10	1.6300	0.2892	0.0878	0.0149	0.1772	0.0540	0.0091
0.15	1.6550	0.2335	0.0918	0.0156	0.1412	0.0555	0.0094

Calculated Residual Manganese
(Equation No. 27)

Logarithms						
Per Cent C	M.F.MnO	M.F.FeO	0.5Log R	K _{Mn}	Log Mn	Per Cent Mn
0.07	8.720	9.299	9.752	0.586	9.083	0.12
0.10	8.732	9.248	9.752	0.586	9.146	0.14
0.15	8.744	9.149	9.752	0.586	9.257	0.18

Table LI (Continued)
Burden Calculations
Weight of Raw Materials Charged

Calculated Residual Phosphorus (Equation No. 19)					
Logarithms					
Per Cent C	M.F. P_2O_5	M.F. FeO^3	K_p	$2Log P$	Per Cent P
0.07	7.944	7.897	3.830	6.235	0.013
0.10	7.959	7.744	3.830	6.385	0.016
0.15	7.973	7.447	3.830	6.696	0.022

Summary of Calculated Slag and Steel Analyses									
C	Steel Mn	P	FeO	SiO ₂	CaO	Slag MnO P ₂ O ₅		R	CaO/SiO ₂ *
0.07	0.12	0.013	23.2	15.1	42.4	6.1	2.0	0.319	2.81
0.10	0.14	0.016	20.8	15.6	43.8	6.3	2.1	0.319	2.81
0.15	0.18	0.022	16.8	16.4	46.0	6.6	2.2	0.319	2.81

*Desulphurizing.

Similarly, by reference to the preceding equations and tables, an appreciation of the important results of changing the total silicious burden with otherwise identical conditions of charging may be obtained:

Table LII
Effect of Silicious Burden Upon Slag and Steel Analyses
 Total Metallic Charge: 350000 Lbs.
 Stone: 9 Per Cent, Dolomite: 4 Per Cent, Hot Metal: 50 Per Cent
 (Variations in Weight of Silica Only)

C	Steel Mn	P	FeO	SiO ₂	CaO	Slag MnO MgO		P ₂ O ₅	Inc. Ox.	R	Slag Wt. Lbs.	Iron Loss Per Cent
0.07	0.17	0.021	16.1	19.4	44.4	6.3	6.4	2.1	5.3	0.360	47300	1.70
0.07	0.14	0.018	19.7	17.4	43.3	6.2	6.2	2.1	5.2	0.340	48500	2.13
0.07	0.12	0.015	22.4	16.1	42.3	6.1	6.1	2.0	5.1	0.325	49700	2.48
0.07	0.09	0.012	26.8	14.0	40.7	5.8	5.8	1.9	4.9	0.300	51600	3.18
0.07	0.08	0.009	32.0	11.8	38.7	5.5	5.5	1.8	4.6	0.270	54300	3.87
0.15	0.19	0.022	17.0	17.0	45.4	6.6	6.6	2.2	5.4	0.320	46300	1.75
0.15	0.14	0.018	20.3	14.6	44.1	6.4	6.4	2.1	5.3	0.290	47500	2.15
0.15	0.12	0.014	24.2	12.6	43.5	6.3	6.3	2.1	5.2	0.260	48400	2.61
0.15	0.10	0.010	28.5	10.0	41.8	6.0	6.0	2.0	5.0	0.225	50300	3.20

These analyses have been found to check well with those of actual practice and lead to three important conclusions:

1. That the *percentage compositions* of lime, magnesia and manganese oxides are not necessarily an indication of the relative basicities of the slags because of iron oxide dilution effects.
2. That increments of iron oxide proceed in much greater proportion than the decrements of silica producing them. It is indicated in the low carbon calculations, for ex-

ample, that the reduction of 3000 pounds (8 per cent) in the silicious charge causes an increase of 10,000 pounds (16 per cent) in the slag oxidation, other factors remaining constant.

3. That the reduction of silica cited above obtains an increased metallic loss of more than 2 per cent referred to the charge via the furnace slag.

The purpose, effect and means for maintaining a favorable acid-base ratio are thus clearly set forth. It is evident that the open-hearth should be concerned with the influence of burdening upon the slag-steel composition as a whole rather than the particular fluctuations of several individual oxides.

With high slag oxidations resulting from a deficiency of silica, a measure of control may obviously be obtained by the careful reduction of limestone burdens as revealed in the following calculations for a constant silicious charge. It has been assumed that little appreciable change of dolomite consumption will occur. The agreement of actual and theoretical slag weights is noteworthy:

Table LIII
Effect of Limestone Burden Upon Slag and Steel Analyses
Metallic Charge: 350000 Lbs. Silica: 8000 Lbs.

Steel			Slag							Inc.	Slag Wt.		Per Cent Iron	Per Cent Stone
C	Mn	P	FeO	SiO ₂	CaO	MnO	MgO	P ₂ O ₅	Ox.	R	Lbs.	Loss	Chg.	
0.07	0.25	0.028	14.0*	21.9	37.7	8.3	8.3	2.8	6.8	0.443	36200	1.15	5	
0.07	0.22	0.026	14.0	19.6	43.2	7.5	7.5	2.4	6.2	0.372	40600	1.30	7	
0.07	0.12	0.012	22.4	16.1	42.3	6.1	6.1	2.0	5.1	0.325	49700	2.40	9	
0.07	0.10	0.009	26.8	15.2	44.6	5.7	5.7	1.9	4.8	0.300	52300	3.06	10	
0.07	0.09	0.007	29.6	14.0	44.0	5.3	5.3	1.8	4.4	0.284	56800	3.75	11	
0.07	0.08	0.006	31.9	13.1	43.4	5.0	4.9	1.6	4.1	0.272	60700	4.32	12	
0.07	0.05	0.005	40.0	10.1	41.1	3.8	3.8	1.3	3.1	0.227	79300	7.07	15	
0.10	0.17	17.6	16.0	42.6	7.0	68—441	...	39100	1.53	6.5	
0.11	0.16	25.0	13.9	42.2	7.5	66—540	...	42900	2.39	6.5	
0.05	0.16	16.6	23.2	39.8	10.0	66—412	...	47000	1.73	8.0	
0.05	0.16	27.0	14.9	42.6	9.0	64—425	...	48100	2.89	8.0	

*By FeO Dilution to End Point.

The proportional addition of burned lime to heats of low acid-basic oxide ratios similarly augments the slag oxidation and invariably results in *decreasing the viscosity* for normal practices because of the attendant increase of iron oxide if the bath is open and sufficient time has been allowed for complete solution. It has been reasonably argued that heavier slags less actively transfer FeO to the bath but, with fusion temperatures (Fig. 2) decreasing in proportion to advancing slag oxidations, it should be difficult to obtain widely different viscosities for similar iron oxide concentration and temperature under

equilibrium conditions. Excepting for higher silica, phosphorus or sulphur melts, the addition of burned lime to the average basic open-hearth heat is more costly than beneficial. The charging of limestone in excess of the minimum amount required for the control of phosphorus is both theoretically and practically unsound, as carefully demonstrated in the historical section of the research, and accomplishes nothing beyond unnecessary expense.

Another of the oxides more familiar to American practices may be profitably studied by calculating the probable consequences of variable manganese or manganese oxide charges under otherwise comparable burdening:

Table LIV													
Effects of MnO Burden Upon Slag and Steel Analyses													
Metallic Charge: 350000 Lbs. Stone: 9 Per Cent Dolomite: 4 Per Cent													
No.	C	Steel Mn	P	FeO	SiO ₂	CaO	Slag MnO MgO		P ₂ O ₅	Inc. Ox.	R	Slag Wt. Lbs.	Iron Loss
1	0.07	0.08	0.018	19.5	17.7	46.4	2.2	6.5	2.1	5.5	0.342	45200	1.96
2	0.07	0.10	0.017	20.7	16.8	44.4	4.3	6.4	2.2	5.3	0.335	47300	2.25
3	0.07	0.12	0.015	22.4	16.1	42.3	6.1	6.1	2.0	5.1	0.325	49700	2.48
4	0.07	0.15	0.014	24.0	15.3	40.5	7.7	5.8	2.0	4.8	0.316	51800	2.76
5	0.07	0.17	0.013	25.1	14.7	38.9	9.4	5.6	1.8	4.6	0.308	54000	3.02
6	0.07	0.19	0.012	26.5	14.1	37.2	10.6	5.3	1.8	4.4	0.300	56300	3.32
7	0.07	0.21	0.010	29.6	12.9	34.0	13.0	4.9	1.7	4.0	0.285	61800	4.07
8	0.07	0.23	0.008	32.0	11.9	31.4	15.1	4.6	1.5	3.8	0.272	66800	4.75
Heats Nos. 4, 6, 8 Charged for Low FeO													
9	0.07	0.24	0.023	14.0	19.6	42.6	8.1	6.1	2.0	5.1	0.372	49300	1.54
10	0.07	0.33	0.021	14.0	19.8	39.4	11.3	5.6	1.9	4.7	0.372	53300	1.66
11	0.07	0.45	0.019	14.0	20.7	32.8	15.6	4.7	1.6	3.9	0.372	64100	1.99
Slags from Actual Operation													
4	0.07	0.17	28.0	12.4	39.7	8.4		20 Heats	
6	0.07	0.19	27.4	12.8	38.6	11.2		11 Heats	
8	0.08	0.23	26.9	13.1	36.4	14.2		4 Heats	
10	0.09	0.32	17.0	16.8	43.1	11.6		49 x 268	

The satisfactory agreement of both slag and steel analyses from plant records with the calculated finishing slags of comparable FeO and MnO contents (Items 4, 6, 8, 10) is sufficient evidence for the general accuracy of the computations. Although the decreasing percentages of calcium oxide fail to show the increasing basicity occasioned by the gradual increments of MnO in the charge, the changing acid-base ratio is followed closely by the slag oxidation. The results show that for otherwise similar charging an augmented manganese burden will so increase iron losses in the slag as to overcome any economy to be derived from higher residual manganese. If, however, excessive slag oxidation is prevented by proportionally higher silicious charges, both optimum furnace yields and greatly increased residual manganese may be so obtained.

For the average case, it may be estimated that each 2000 pounds of MnO (0.6 per cent referred to charge) will achieve approximately 0.09 per cent higher residual manganese with a 9 per cent stone burden and 350,000 pounds metallic charge for an alloy saving of \$.135 ($9 \times \0.015) per ton of ingots. At present (1934) raw material prices, the addition of 5 tons of 14 per cent Mn ore (Wyalla) at \$13.25 (less \$8.55 for replaced charging ore) to produce 2000 pounds of MnO would cost \$.166 per ton of ingots. Since the blast furnace burden (with 15 per cent open-hearth slag yielding 1.90 per cent Mn iron) consumes slightly less than half the total slag production, only fifty per cent of the initial 5-ton addition would be required to maintain sufficient manganese in the iron (2.80 per cent) to obtain 12 per cent MnO in the open-hearth slags at a cost of \$.083 per ton and a net economy of \$.05 per ton. The full addition would be necessary for one day each month during which open-hearth slag should be removed from the blast furnaces to prevent the pyramiding of phosphorus.

On the other hand, with a 50 per cent charge of 1.90 per cent Mn hot metal as at present yielding 4000 pounds of MnO, a slag volume reduced from 50,000 to 37,000 pounds would increase the MnO directly to 11.0 per cent. With such MnO concentrations, a residual manganese of 0.30 per cent could be expected with 15 per cent FeO for a direct saving in alloys alone of \$0.18 per ton of ingots. The required slag weight may be very simply obtained by reducing the original stone charge from 9 per cent to 5.0 per cent with all the other attendant economies of increased production, furnace and alloy yields, heating and fluxes as previously reported for the campaign of No. 69 furnace in 1930. (Table XXXIX).

In passing, it may also be suggested that the manufacture of the higher carbon, sluggishly rimming steels could probably be improved by obtaining the desired manganese content as residual in the bath through employing low volume, 11 per cent to 12 per cent MnO oxide slags. Since under these circumstances the iron oxide concentration of the bath should not be decreased, it seems reasonable to suppose that the absence of a large, deoxidizing addition of ferro-manganese to the bath, should result in a definitely more effective rimming action in the molds. No aluminum may be added to the ladle for control purposes: like many steels, they must be made in the furnace.

The influence of the two basic oxides, CaO and MnO, upon

Cent	
t. Iron	Loss
1.96	
2.25	
2.48	
2.76	
3.02	
3.32	
4.07	
4.75	
1.54	
1.66	
1.99	

Heats
Heats
Heats
x 268

open-hearth slags has been discussed in detail, but the third and most basic of the triumvirate is seldom determined and less frequently investigated. Magnesium oxide is present in all basic slags where dolomite (20 per cent MgO) is used for bottom making. The respective basicities of the three oxides are in proportion to the number of mols present:

Oxide	Mol Wt.	Per Cent	Mols	Per Cent SiO ₂ (2RO.SiO ₂)	Per Cent P ₂ O ₅ (3RO.P ₂ O ₅)
MnO	72	1.0	0.0139	0.42	0.66
CaO	56	1.0	0.0179	0.54	0.85
MgO	40	1.0	0.0250	0.75	1.18

Thus, while increments of the oxide probably decrease the viscosity, it appears that high MgO contents would permit lower slag volumes for highly acid charges whereas, with a deficiency of acids, a minimum of MgO would decrease the iron oxide concentrations for the same charge. Although the ensuing calculations are entirely speculative and without regard to the price of materials, it is interesting to consider the slag effects resulting from the interchange of limestone and dolomite in the furnace burden:

Table LV
Effect of MgO Upon Slag and Steel Analyses
Metallic Charge: 350000 Lbs. Total Silica: 8000 Lbs.

No.	Steel			Slag							Inc.	Per Per			
	C	Mn	P	FeO _s	SiO ₂	CaO	MnO	MgO	P ₂ O ₅	Ox.	R	Slag Weight	Iron Loss	Cent Stone	Cent Dol.
1	0.07	0.12	0.015	22.4	16.1	42.3	6.1	6.1	2.0	5.1	0.325	49500	2.5	9.0	4.0
2	0.07	0.13	0.017	20.3	16.4	50.0	6.2	0.5	2.1	5.2	0.336	48700	2.2	13.0	0.0
3	0.07	0.11	0.014	24.1	16.1	27.2	6.0	18.1	2.0	5.0	0.315	49700	2.7	0.0	13.0
4	0.07	0.15	0.018	20.3	18.0	28.4	6.8	18.9	2.3	5.6	0.336	44400	2.0	0.0	12.0
5	0.07	0.16	0.019	20.3	20.0	0.5	7.5	43.4	2.5	6.2	0.336	40000	1.8	Mg CO ₂ :10.5	

By replacing raw dolomite with crushed limestone for repairing the slag lime, one plant was able to reduce the MgO content of the slags from 7-8 per cent to below 3 per cent with satisfactory phosphorus and sulphur removal, slag control and normal bottom repairs. A more viscous and, of course, higher lime slag was produced for corresponding iron oxide analysis. It was found advisable, however, to substitute dolomite again immediately before shutting down the furnaces for protracted periods to avoid slacking the bottoms. The relative amounts of acid material in the charge and the delivered price of limestone and dolomite are the controlling factors of the

situation which exemplifies another possible refinement of practice contributing to general economy.

Although domestic ores normally produce a low phosphorus basic iron, the recharging of open-hearth slags at the blast furnaces for economy of lime and manganese causes a gradual pyramiding of phosphorus which, if continued indefinitely, might be expected to modify the open-hearth slags with otherwise constant burden as follows:

Table LVI
Effect of P_2O_5 Burden Upon Slag and Steel Analyses
Metallic Charge: 350000 Lbs. Stone: 9 Per Cent Dolomite: 4 Per Cent

No.	Steel			Slag							Inc. Ox.	R	Slag Weight Lbs.	Iron Loss Per Cent
	C	Mn	P	FeO	SiO ₂	CaO	MnO	MgO	P ₂ O ₅					
1	0.07	0.11	0.009	24.2	15.9	41.9	6.0	6.0	1.0	5.1	0.315		50200	2.70
2	0.07	0.12	0.015	22.4	16.2	42.3	6.1	6.1	2.0	5.1	0.325		49700	2.48
3	0.07	0.12	0.020	21.0	16.2	42.5	6.1	6.1	3.1	5.1	0.332		49500	2.32
4	0.07	0.13	0.024	19.6	16.2	42.6	6.1	6.1	4.1	5.1	0.339		49400	2.15
5	0.07	0.15	0.033	16.9	16.4	43.1	6.2	6.2	6.2	5.2	0.353		48700	1.83
6	0.07	0.18	0.048	14.3	16.5	43.4	6.2	6.2	8.3	5.2	0.367		48300	1.54
7	0.07	0.18	0.053	14.0*	16.1	42.5	6.1	6.1	10.2	5.2	0.382		49400	1.53
8	0.07	0.18	0.059	14.0*	15.8	41.6	5.9	5.9	11.9	5.2	0.395		50500	1.58
9	0.07	0.18	0.063	14.0*	15.4	40.5	5.8	5.8	13.4	5.3	0.410		51800	1.62
Comparable Slags from Actual Practice														
2	0.07	0.17	0.012	22.6	16.2	42.1	6.7	6.8	1.8	5.7	0.322		Data	
5	0.06	0.27	0.035	18.7	13.7	44.2	8.1	5.8	5.4	4.5	0.300		Herty	
9	0.06	0.22	0.066	15.2	11.2	34.8	7.3	13.6	15.0	3.2	0.307		Colclough	

*By FeO Dilution to End Point.

The comparability of actual and calculated analyses from similar practices with variable phosphorus charges continues to support the relative accuracy of the acid-basic slag oxidation theory. The desirable effect of phosphorus oxide in reducing the iron oxide content of the slags in almost direct proportion is obviously counterbalanced by accompanying, objectionable increments of residual phosphorus. The control of this readily oxidized element is comparatively simple and the final concentration in the bath may be decreased by any of a number of methods:

1. Reduction of the amount present in the hot metal by readjustments of the blast furnace ore mixture.
2. Reduction of the total iron charge in the open-hearth.
3. Mixture of basic with low phosphorus Bessemer iron.
4. Sufficient flushing of the furnaces at the proper stage of the heat.
5. Maintaining the FeO content of the slag above the

critical rephosphorization point for the particular percentage of P_2O_5 .

6. Increasing the slag volume to increase the oxidation and decrease the P_2O_5 content by dilution.

The inclusion of high phosphorus ores and slags in the blast furnace burden progressively and deleteriously affects both the economy and quality of stationary open-hearth operation, especially when mixture costs prohibit a sufficiently high iron and ore charge to obtain adequate flushing. The maintenance of higher stone charges or the addition of burned lime retards the speed of operation, increases the slag volume, oxidation and metallic loss and reduces both residual manganese and alloy efficiencies. The possibilities for off-grade heats are enhanced and surface quality suffers unless the consumption of manganese, silicon and aluminum is increased to obtain proper deoxidation.

When it is realized that from fifty to seventy-five per cent of the total phosphorus charged in the blast furnace carrying a 15 per cent open-hearth slag burden is obtained from and gradually pyramided in the slag, determination of the actual economy of this procedure to the plant as a whole requires a careful and detailed investigation. The balance existing for a given ore mixture, the amount of slag charged and the phosphorus distribution may be approximated as shown hereafter if it be assumed that the iron content of the burden be held constant by variations of low phosphorus ore following the fluctuations of the slag charge.

An equilibrium between blast furnace and open-hearth operations requires that the *weight of phosphorus in the iron burden* equal the *weight of phosphorus in the open-hearth slags for conditions of simultaneous practices*. It is convenient to know the ratio of the ferrous burden (ores and slag) to iron produced and the total amount of phosphorus introduced by the ores for the particular circumstances.

Given:

$$R = \frac{\text{Wt. Iron Produced}}{\text{Wt. Ferrous Burden}} = 55 \text{ per cent (Present Data)}$$

P_1 = P in the iron

P_o = P in P_1 from ores = 0.100 per cent

P_s = P in O.H. slag

P_R = P residual in steel = 0.020 per cent

Per Cent Slag = Per Cent slag mix in burden

Slag Wt. = average wt. of O.H. slag = 50000 pounds

Per Cent Iron = Per Cent iron charge in O.H. = 50 per cent

Total Chg. = avg. wt. of metallic charge in O.H. = 350000 pounds

Per Cent P_2O_5 = 2.3 (Per Cent P_s)

Then:

$$P_s = (\text{Per Cent } P_i - \text{Per Cent } P_R) (\text{Per Cent Iron}) (\text{Tot. O.H. Chg.}) \quad (29)$$

$$\text{Per Cent } P = \frac{P_s}{\text{O.H. Slag Wt.}}$$

By Heats:

$$P = \frac{(\text{Per Cent Iron}) (\text{Tot. O.H. Chg.}) (\text{Per Cent Slag}) (\text{Per Cent } P_s) + R (\text{Per Cent } P_o) (\text{Per Cent Iron}) (\text{Tot. Chg.})}{R} \quad (30)$$

According to the premise that the pounds of phosphorus in the open-hearth slag must equal the pounds of phosphorus reduced to the hot metal from the slag and ore burden, equation (29) equals equation (30). The product, (Per Cent Iron) (Tot. Chg.), being common to all terms of the equations, may be eliminated and the expression becomes:

$$\text{Per Cent } P_i - \text{Per Cent } P_R = \frac{(\text{Per Cent Slag}) (\text{Per Cent } P_s)}{R} + \text{Per Cent } P_o \quad (31)$$

If Per Cent P_i = 0.300 Per Cent, Per Cent P_s = 0.980 Per Cent
 Per Cent P_R = 0.020 Per Cent, Per Cent P_o = 0.100 Per Cent
 R = 55 Per Cent, Per Cent Iron = 50 Per Cent

Substituting: (Per Cent Slag) = 10.1 Per Cent
 Per Cent P_2O_5 = 2.25 Per Cent

Estimation of the progressive slag balance points for these ore mixtures and 9 per cent stone charges is as follows:

Table LVII
Open-Hearth Blast Furnace Phosphorus Balance

Per Cent Hot Metal Charge	O.H. Slag Weight Lbs.	Per Cent P_i from Ore Mix	Per Cent O.H. Slag Chgd. at B.Fce.	Per Cent P in Iron	Per Cent P_2O_5 in O.H. Slag	Resid. P with 20 Per Cent FeO
50	50000	0.100	0.0	0.120	0.5	0.007
50	50000	0.100	7.0	0.200	1.5	0.012
50	50000	0.100	10.1	0.300	2.3	0.018
50	50000	0.100	11.6	0.400	3.1	0.022
50	50000	0.100	12.4	0.500	3.9	0.024
50	50000	0.100	13.6	0.750	5.9	0.028
50	50000	0.100	14.1	1.000	7.9	0.033
50	50000	0.100	15.0	2.000	16.0	0.051

While the criteria above 10 per cent slag charge are manifestly unsuited to American steel making practices, the phosphorus increment with even a 15 per cent slag burden is fortunately slow because half

the open-hearth slag production is put over the dump. An example typical of the practice is listed for a basic hot metal division operating under these conditions:

Table LVIII
Open-Hearth Slag—Hot Metal Phosphorus Balance
Slag Wt.: 50000 Lbs. Slag Chg.: 15 Per Cent Hot Metal Chg.: 50 Per Cent

Date		Hot Metal Analyses			P ₂ O ₅ Slag	P in Steel at 20 Per Cent FeO
		Mn	Si	P Per Cent		
May	10	1.78	1.06	0.188	1.60	0.015
	15	1.91	1.26	0.218
	20	1.95	1.06	0.239	2.15	0.017
	25	1.60	1.04	0.261
	30	1.74	1.24	0.259	2.35	0.018
June	5	1.71	1.37	0.253
	10	1.70	0.93	0.285	2.60	0.019
	15	1.58	1.14	0.287
	20	1.49	0.71	0.344
	25	1.74	1.16	0.308	2.80	0.020
July	30	1.67	0.78	0.283
	5	1.88	0.88	0.333
	10	2.05	1.05	0.364	3.30	0.022
	15	1.97	1.19	0.390
	20	1.97	1.12	0.390	3.50	0.023

It has thus required approximately two months with 15 per cent slag charge to increase the phosphorus in the iron by 0.200 per cent and in the slag by 2.0 per cent. If then the open-hearth slag is completely removed from the blast furnace charge once each month, the bins cleared and *all the slag production for the first fifteen days be stocked* for charging, the phosphorus increment should be held to 0.100 per cent above that furnished by the ores during the period. When changing burdens, 24-hours' supply of the lowest phosphorus slag, previously stocked for the purpose, will prevent interruption of the practice for several months at a time.

The steel-iron balance for manganese with slag charging at the blast furnace may be similarly figured with the addition of a term for the manganese in the open-hearth charge, "M_x", referred to the weight of hot metal:

$$\% \text{ Slag} = \frac{(\text{Per Cent } M_i - \text{Per Cent } M_o - \text{Per Cent } M_R + \text{Per Cent } M_x)}{\text{Per Cent } M_s} \quad (55)$$

(32)

It should be noted that the "P_x" term is unnecessary in the phosphorus equation because the phosphorus charged with the open-hearth scrap is normally equivalent to the residual amount.

Table LIX
Open-Hearth Blast Furnace Manganese Balance

Slag Wt.: 50000 Lbs.			Slag Chg.: 15 Per Cent		Hot Metal Chg.: 50 Per Cent		
Per Cent Hot Metal Charged	Lbs. O.H. Slag Weight	Per Cent Mn from Ore	Per Cent Mn from Scrap	Per Cent O.H. Slag Chgd. at B.Fce.	Per Cent Mn in Iron	Per Cent MnO in O.H. Slag	Resid. Mn with 20 Per Cent FeO
50	50000	0.45	0.30	7.2	0.50	3.3	0.05
50	50000	0.45	0.30	9.6	1.00	5.4	0.11
50	50000	0.45	0.30	10.6	1.25	6.3	0.13
50	50000	0.45	0.30	11.4	1.50	7.4	0.15
50	50000	0.45	0.30	12.0	1.75	8.3	0.18
50	50000	0.45	0.30	12.3	2.00	9.4	0.20
50	50000	0.45	0.30	12.7	2.25	10.5	0.22
50	50000	0.45	0.30	13.0	2.50	11.5	0.25
50	50000	0.45	0.30	13.3	3.00	13.5	0.28
50	50000	0.45	0.30	13.7	3.50	15.8	0.33

Mathematical manipulation of the manganese equations suggests that small variations of the manganese burden in either operation exerts an important influence upon the balance. It is possible to calculate that with 15 per cent slag burden, 1.90 per cent Mn hot metal, 50 per cent metal charge, 8.1 per cent MnO and 50,000 lb. slag weight, an iron-steel making equilibrium will exist if 0.07 per cent Mn is obtained from the ore mix. In confirmation thereof a test blast furnace run produced 1.85 per cent Mn from a 15 per cent slag charge averaging from 8.0 to 8.5 per cent MnO with no other manganiferous burden. The control of manganese between the specified limits may be achieved by varying the manganese ore burdens while the minimum phosphorus concentration can only result from eliminating open-hearth slag from the charge.

It being demonstrable that excess phosphorus adversely affects the open-hearth practice and that the economy of utilizing the iron and manganese contents of the steel-making slags definitely reduces blast furnace mixture costs—final decision as to the ultimate advantage to the plant rests with accurate cost accounting of the possible methods of procedure.

Cost credits accruing to the blast furnace have been figured from actual burden calculations for the *replacement* of manganiferous ore (Wyalla) by open-hearth slag as follows:

Mn Increment in Hot Metal Per Cent	O.H. Slag Credit per ton of Pig Iron	
	1930	1932
0.10	\$0.050	\$0.057
0.20100	.114
0.30150	.171
0.40200	.228
0.50250	.285
1.00500	.570
2.00	1.000	1.140

Operating economies in the open-hearth must be obtained through decreased stone charging made possible by the lower phosphorus hot metal resulting from the reduction of the slag burden of the blast furnaces. With 5.5 per cent limestone burden and a slag volume consequently reduced from 50000 to 38000 pounds at 16 per cent FeO, the manganese required in 50 per cent hot metal to produce 8.0 per cent MnO will be decreased from 1.85 to 1.40 per cent. If, of this amount, 0.10 per cent is residual in the ore burden and, since 5 per cent open-hearth slag yielding 0.40 per cent Mn could still be charged without increasing the phosphorus in the iron above 0.160 per cent nor the P_2O_5 above 1.5 per cent, a net percentage of 0.90 Mn must depend upon manganiferous ores.

According to the previous tabulation, 0.90 per cent Mn in the iron from such sources would exact a penalty of \$0.52 per ton of pig iron amounting to \$0.30 per ton of ingots with 50 per cent metal charge. From the experimental run of No. 69 Furnace with 5.0 per cent stone charge previously reported in detail (Table XXXIX), the listed improvements of practice may be conservatively estimated to accomplish the following savings:

1. Production increased by 8.3 per cent for 1000 tons in five weeks: no estimate.
2. Fuel consumption reduced by 7.7 per cent or an average of 2.3 gallons of oil per ton: \$0.06 per ton.
3. Decreased fluxes: \$0.11 per ton.
4. Decreased ferromanganese consumption: \$0.10 per ton.
5. Furnace yields improved by 1.8 per cent through less scrap and oxidation loss: \$0.25 per ton.
6. Total approximate credits: \$0.52 per ton.

In view of these findings, an apparent economy of \$0.30 per ton of ingots through charging 15 per cent open-hearth slag at the blast furnace may well result in a consequent expense to the steel-making department of approximately \$0.50 per ton if the natural advantages of a low phosphorus, low silicon charge are disregarded in burdening the open-hearth furnaces.

There are two stock objections to lower limestone charges in the basic open-hearth where raw materials permit:

1. That atmospheric oxidation of the slag is accelerated by its decreased volume although the surface area remains constant.
2. That by some devious process never definitely described, slags of greater volume, other things being equal, produce

steel of better internal and external quality, although comparable summaries of product yields of many grades of steel fail to confirm such suspicions.

In refutation it may be advanced that, as far as these studies have proceeded, the same equilibria appear to hold for slag oxidation, residual manganese and phosphorus within the limits of the slag volumes investigated. The metallurgical processes are governed by the laws of physical chemistry and, given the same conditions of temperature, bath and slag analyses, it is difficult to discover any theoretical or practical objections to reducing the slag volume to the minimum designed for most economically effecting the required physical and chemical control.

The issue is likewise confused with the proposition that increased stone charges necessarily require low slag volumes and that low percentages of calcium oxide denote insufficient basicity. In the first case, the slag volume may be arbitrarily and indefinitely increased by subsequent furnace additions of burned lime or ground limestone if necessary—without penalizing the operating efficiency by heavy stone charges. In the second instance, the relative basicity of the slags can be determined only from complete analyses. The iron oxide content is a reliable barometer of changing acid-base ratio and, beyond its invaluable functions of controlling residual elements and slag oxidation, the actual basicity should otherwise be metallurgically unimportant.

Calculation of Residual Iron Oxide from Manganese Equilibria

It now becomes possible to reconsider briefly the equilibria proposed for the carbon, slag oxidation, residual iron oxide reaction. This has been assumed to have the form

$$\text{FeO}_B = \frac{(K_T)(\text{FeO}_s)}{C}$$

as developed on page 346 and calculated over the working range in Table VI.

Dissatisfaction with this conception of the reaction arises from three primary causes:

- a. Determinations of iron oxide in the steel at higher carbons are usually in excess of those calculated from corresponding data.

- b. Alloy losses for higher carbon heats are considerably above the proportional amount suggested by the respective bath oxidations (Table XXVIII), although this is partially explained by increased slag reactivity through increments of the silica content in the ladle.
- c. In basic slags of the $n\text{RO} \cdot \text{SiO}_2$ type, formulae for the elimination of phosphorus and manganese from the bath seem not to require a carbon term.

It may be reasonably suggested, therefore, that the concentration of residual iron oxide in the basic open-hearth bath follows the simple distribution law of Nernst:

$$\frac{\text{FeO}_s}{\text{FeO}_B} = K$$

and that the influence of carbon is confined principally to its definite and measurable effect upon the slag oxidation (Equation 9) under equilibrium conditions.

The difficulty of obtaining accurate and representative determinations of residual iron oxide renders it desirable to develop the particular equilibrium constants for slag and metal by methods other than direct analysis. From the physico-chemical laws previously employed, it may be shown that:

$$(1.) \quad \frac{\text{Per Cent FeO}_s}{\text{FeO}_B} = K_{2970} = \frac{26.1}{0.155} = 168.4 \text{ (Table V)} \quad (34)$$

(The molecular fractions of FeO and MnO are directly proportional to their percentage compositions: Fig. 6.)

$$(2.) \quad \frac{\text{Per Cent MnO}}{(\text{Per Cent FeO}_s)(\text{Mn})} = 2.27 \quad (\text{Equation 27})$$

(3.) Substituting for Per Cent FeO_s from (1) in (2):

$$\text{FeO}_B = \frac{(\text{Per Cent MnO})}{(381)(\text{Mn})} \quad (35)$$

This suggests that, under equilibrium conditions near 2950 degrees Fahr., the oxidation of the bath is proportional to the ratio of MnO to Mn. Empirical data for the variations of these related criteria and carbon under similar conditions of temperature have been averaged from more than a thousand tapping tests as follows:

Table LX
Variations of Carbon and Calculated Residual Iron Oxide

No. Hts.	Per Cent C	Per Cent Mn	Per Cent FeO _s	Per Cent MnO	Per Cent Residual FeO _n		
					Table VI	Equation (35)	Equation (34)
96	0.05	0.148	25.0	6.77	0.154	0.123	0.148
96	0.06	0.144	24.7	6.96	0.128	0.130	0.147
96	0.07	0.161	22.4	7.14	0.099	0.119	0.133
96	0.08	0.174	20.7	7.43	0.079	0.114	0.123
96	0.09	0.177	21.4	8.03	0.073	0.122	0.127
48	0.10	0.182	20.6	7.44	0.064	0.110	0.122
48	0.11	0.184	19.9	7.88	0.056	0.115	0.118
48	0.12	0.185	21.2	7.49	0.055	0.109	0.126
48	0.13	0.193	20.7	7.73	0.049	0.108	0.123
48	0.14	0.202	19.3	8.08	0.043	0.107	0.114
48	0.15	0.192	20.9	7.82	0.043	0.109	0.124
48	0.16	0.193	21.8	7.45	0.042	0.104	0.129
48	0.17	0.209	19.1	7.83	0.035	0.101	0.113
48	0.18	0.193	20.1	7.40	0.035	0.103	0.119
48	0.19	0.202	19.9	7.58	0.033	0.101	0.118
48	0.20	0.199	18.8	7.31	0.029	0.096	0.111
*	0.50	0.310	12.0	8.00	0.007	0.069	0.071

*(From Mn-MnO Equilibrium, Fig. 11.)

While the agreement of the residual FeO data calculated from equations (34) and (35) is excellent and greatly in excess of that from Table VI, the only direct evidence available to support it was obtained by questionable analytical procedure and is too limited to be convincing:

No. Hts.	C	Steel		FeO _s	SiO ₂	Slag		
		Mn	FeO _n			CaO	MnO	P ₂ O ₅
11	0.052	0.119	0.155	26.1	14.0	40.8	6.8	1.8

Since the distribution coefficient was set up from this source (Equation 34) the value for residual iron oxide will check exactly, of course, with that determined as 0.155 per cent FeO_B. It is at least interesting that substitution in the manganese equation (35) gives closely similar results:

$$\text{Per Cent FeO}_n = \frac{(\text{Per Cent MnO})}{381(\text{Mn})} = \frac{6.8}{(381)(0.119)} = 0.150 \text{ Per Cent} \quad (35)$$

The suggestion is presented for what it may be worth. It is to be hoped that future investigations may definitely establish the correct equation for the reaction as well as the equilibrium constant.

SUMMARY

With an intimate knowledge of the many limitations and defects of this research, its publication has been accompanied with no little hesitation and reluctance. If it may serve in any respect as a

basis for further investigations, it will have more than justified its purpose. The summation of its results is, for the most part, suggestive rather than conclusive.

1. The very important effects of fluctuations of hot metal analyses upon open-hearth slags, temperatures, economy and steel quality have been reported. Variations in silicon below the optimum range have been shown to adversely influence tapping temperatures and deoxidation practices by upsetting the normal slag balance and oxidation (Tables VIII, IX).
2. The constant for one conception of the iron-oxide-carbon reaction has been tentatively developed:

$$\frac{(\text{FeO}_\text{B})(\text{C})}{\text{FeO}_\text{S}} = K_{\text{FeO}} = 0.00031 \quad (\text{Table VI})$$

3. The correction factor for the effect of Fe_2O_3 upon the total equivalent slag oxidation has been expressed:

$$\text{FeO}_\text{S} = 1.51 (\text{total iron}) \quad (\text{Table VII})$$

4. The influence of varying slag oxidations upon analysis control and chipping expense has been demonstrated (Tables XIV, XV).
5. The production and habits of rimming steels have been discussed in detail. (Tables XVI-XXI, incl.).
6. The applications of variable deoxidation practices to maintain consistent rimming qualities have been suggested. (Tables XXII-XXIV, incl.).
7. An investigation of the proportional deoxidation necessary for several grades of killed steel has been reported. (Tables XXV-XXVIII, incl.).
8. The proposition is advanced that the manufacture of rimmed or killed steels of satisfactory quality requires the proper empirical adjustment of deoxidation practices to bath and slag oxidation, while economies in furnace and alloy yields and uniformity of operation require maintenance of a minimum practical slag oxidation.
9. The development of slag control in 1929 has been reviewed, including typical examples of heats with high silicon metal, manganese ore, and Bessemer slag, together with the influence of furnace atmospheres. (Tables XXX-XXXIII, incl.).

10. The degree of control of slag oxidation exercised by changing lime-silica ratios with constant burdening has been set forth. (Table XXXIV and Fig. 1).
11. Methods for the positive and negative corrections of slag oxidation by the respective additions of burned lime or silica (in the presence of sufficient carbon to complete the reaction) have been described. (Tables XXXVI-XXXVII, incl.).
12. The many operating advantages attendant upon reduced stone charges in the open-hearth have been reported in detail. (Table XXXIX).
13. Continuation of slag-metal reactions in the ladle through increments of silica from additions and refractories have been suggested in reference to rephosphorization and deoxidation practices. (Table XL).
14. Inaugurating a discussion of the applications of physical chemistry to the slag-metal equilibria, study of the several viscosity theories suggests fluidity to be a result, not a cause of slag oxidation. (Fig. 2).
15. It has become evident that examination of these reactions requires simultaneous consideration of corresponding slag and steel samples (proposed by Colclough) under conditions of potential equilibrium. Subsequent investigations have therefore been confined to tests taken at tapping immediately before furnace additions.
16. Contemplation of graphs of the mol fractions of iron oxide plotted with those of excess bases (suggested by Stead and Colclough) above the amounts required to combine with P_2O_5 and SiO_2 finds a mineral hypothesis convincing. (Fig. 3).
17. Fletcher's neutral balance between acid and basic *oxygen* approximates a straight line relationship which becomes more regularly expressed with ordinates for the mol fractions of FeO and the ratio of acid and basic *oxides*. (Fig. 3).
18. There appears to be a regular trend of equivalent slag oxidations toward balanced equilibrium with the acid and basic components of the slag in which both iron oxides assume acid characteristics (proposed by Stead) and the individual components enter into the relationships in proportion to their mol fractions.
19. These equilibria for the present data may be approximately expressed as follows when "R" is the ratio described above:

Residual Carbon
Per Cent

Equation

0.07

$$\text{M.F. FeO}_s = 0.710 - 1.60R$$

(1)

0.15

$$\text{M.F. FeO}_s = 0.490 - 1.09R$$

(2)

20. The variations of the mol fractions of FeO_s and MnO_s may be shown to be directly proportional to their percentage compositions:

$$\text{Per Cent FeO}_s = 111(\text{M.F. FeO}) + 1.2 - \frac{\text{M.F. MnO}}{0.00845} \quad (3)$$

$$\text{Per Cent MnO} = \frac{\text{M.F. MnO}}{0.00845} \quad (\text{Fig. 5})$$

21. It follows then that the per cent FeO may be expressed in terms of "R":

Residual Carbon
Per Cent

Equation

0.07

$$\text{Per Cent FeO}_s = 80.0 - 177.6R$$

(5)

0.15

$$\text{Per Cent FeO} = 55.4 - 121.0R$$

(Fig. 6)

22. Assuming these equations to be simultaneous, it is indicated that the formula for the carbon-slag oxidation reaction may be written:

$$(C^{422})(\text{Per Cent FeO}_s) = K_{2925} = 1.173 \quad (7)$$

23. The variation of the constant in equation (7) follows the straight line formula:

$$K = 2.456 - 5.35R \quad (8)$$

24. Combination of equations (7) and (8) suggests the following expression for the general form of the $\text{C-FeO}_s\text{-R}$ reactions:

$$(C^{422})(\text{Per Cent FeO}_s) = 2.456 - 5.35R \quad (9)$$

25. For convenience of manipulation, the values for C^{422} have been reproduced graphically in Fig. 7.

26. Probably because of oxidizing atmospheres, the end points of the above equilibrium, regardless of increasing acidity, have been experimentally determined for basic open-hearth practice as follows:

Residual Carbon
Per Cent

FeO_s End Point
Per Cent

0.07

14.0

0.15

12.0

0.50/0.80

8.0

27. It is suggested that the equilibria will hold to below 5 per cent FeO_s under the reducing conditions of the basic electric furnace.

28. Evidence is presented to show that the reduction of iron oxide from a basic slag by silicious additions will take place only in the presence of sufficient carbon to complete the reaction which is definitely a chemical, not a dilution effect, as correctly proposed by Campbell.
29. Unsuccessful attempts were made to distinguish between the relative activities of slags with identical equivalent iron oxides but high and low Fe_2O_3 . (Table XLII).
30. It is reported that logarithmic solution for the coefficients of the conventional formula for the oxidation of phosphorus gives in effect the following reaction:



Attempts to check this by direct determination showed that the careful and complete analysis of a synthetic high phosphorus slag totaled one hundred per cent only when the phosphorus was reported as P_2O_5 .*

31. The equilibrium constant for the P_2O_3 equation was determined as follows:

$$\frac{(\text{P}_2\text{O}_3)}{(\text{FeO}^2)(\text{P}^2)} = K_{2925} = 6761 \quad (19)$$

32. The reaction constants for the oxidation of manganese were similarly determined. They may be adequately expressed for usual conditions with or without a term for basicity:

$$\frac{\text{MnO}}{(\text{Mn})(\text{FeO})} = K_{2925} = 2.21 \quad (27)$$

$$\frac{\text{MnO}}{(\text{Mn})(\text{FeO})(\text{R}^{\cdot 5})} = K_{2925} = 3.86 \quad (28)$$

The exponent of "R" agrees with that first reported by Herty (15) for "available base."

33. The necessary basicity for the elimination of sulphur is indicated by the report of Mr. William E. Steiner and confirmed by the present data.
34. A simple and convenient method for calculating slag weights and analyses from an exact knowledge of the materials charged is presented. This depends, first, on determining the acid-

*See footnote page 374.

basic oxide ratio, "R," from the pound-mols in the burden and then estimating the total slag weight for the required tapping carbon by dividing the total oxide burden by 100-per cent FeO_s from equation (9). (Table LI).

35. The approximate effects of varying the SiO_2 , CaO , MnO , MgO , and P_2O_5 contents of the burden upon slag oxidation and bath analysis have been calculated. (Tables LII to LVI, incl.).
36. The close approach of these estimated analyses to those for similar burdens from actual practice confirms both the method and the equivalent slag oxidation theory described under items Nos. 3 and 18.
37. The extreme importance of the phosphorus burden of the blast furnaces in controlling open-hearth practices and costs is described in detail.
38. A convenient formula for establishing operating equilibrium for phosphorus charges between blast furnace and open-hearth is presented:

$$\text{Per Cent Slag} = \frac{(R) (\text{Per Cent } P_I - \text{Per Cent } P_R - \text{Per Cent } P_o)}{\text{Per Cent } P_s} \quad (31 \text{ and Table LVII})$$

39. A similar discussion and formula for the manganese-blast furnace-open hearth balance is offered:

$$\% \text{ Slag} = (R) \frac{(\text{Per Cent } M_I - \text{Per Cent } M_o - \text{Per Cent } M_R + \text{Per Cent } M_x)}{\text{Per Cent } M_s} \quad (32 \text{ and Table LIX})$$

40. The advantages of lower limestone charges for improved plant operations and lower costs are advocated. In general it appears that, beyond their metallurgical utility in controlling slag oxidation and metalloids, stone charges may be reduced to the minimum consistent with the required phosphorus elimination.
41. For optimum plant practice, the burdening of blast furnaces and open-hearths should be considered together in detail. Apparent sacrifices of cost at the former are often favorably reflected in the steel-making.
42. It is suggested with reservations that the concentration of iron oxide residual in the basic open-hearth bath may follow the simple distribution law of Nernst, and that the influence of

carbon may be confined to its measurable effect upon the slag oxidation alone.

43. A simple formula for the calculation of residual iron oxide from manganese and MnO has been tentatively employed:

$$\frac{(\text{Per Cent MnO})}{(\text{FeO}_B)(\text{Mn})} = K_{2900} = 381 \quad (35)$$

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In an investigation extending over as many years as this one, it is difficult to acknowledge the contributions of all the many individuals without whose assistance the work could not even have been attempted. It is desired, however, to express an especial indebtedness to the following gentlemen of the Bethlehem Steel Company:

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Slag-Steel Data

Data No.	Mol Factors	No. 1	No. 2	No. 3	No. 4	No. 5 Per Cent	No. 6	No. 7	No. 8
C	0.06	0.08	0.08	0.06	0.08	0.05	0.05	0.07
Mn	0.14	0.18	0.18	0.14	0.16	0.14	0.12	0.15
P	8.16	9.83	9.73	10.50	11.08	12.32	15.97	11.71
FeO	5.79	6.86	7.33	7.72	10.97	11.58	11.77	7.29
Fe ₂ O ₃	0.0139	15.97	19.72	19.62	20.92	25.90	27.97	31.15	21.57
SiO ₂	0.0167	20.63	17.67	16.99	17.27	14.76	13.35	11.56	16.46
P ₂ O ₅	0.0071	2.28	1.79	2.00	2.20	1.71	2.59	2.59	1.62
Cr ₂ O ₃	0.0066	0.41	0.34	0.40	0.50	0.23	0.39	0.60	0.44
TiO ₂	0.0125	1.54	1.89	1.90	1.49	1.87	1.65	1.40	1.40
V ₂ O ₅	0.0055	3.02	1.88	2.27	2.52	1.93	3.13	2.99	2.08
Al ₂ O ₃	0.0100	0.65	1.45	0.75	0.95	0.56	0.75	0.75	1.32
Mols Total Acids	0.4045	0.3573	0.3409	0.3483	0.2991	0.2913	0.2549	0.3301
Mols-FeO ₃	0.2219	0.2739	0.2725	0.2907	0.3597	0.3883	0.4427	0.2994
CaO	0.0179	41.90	40.55	40.50	41.90	41.80	37.84	38.37	42.72
MnO	0.0139	6.25	7.33	8.02	6.24	6.29	7.01	5.95	5.95
MgO	0.0250	7.98	8.80	7.54	6.76	6.08	6.44	6.02	7.35
Mols Total Bases	1.0343	1.0456	1.0230	1.0033	0.9853	0.9233	0.9178	1.0291
R	0.391	0.342	0.333	0.347	0.304	0.316	0.278	0.322
Mol Fract. Avail. Base	0.1797	0.2500	0.2538	0.2330	0.2783	0.2785	0.2957	0.2692
Mol Fract. FeO ₃	0.1336	0.1632	0.1665	0.1768	0.2188	0.2574	0.2741	0.1922

Slag-Steel Data

Data No.	Mol Factors	No. 9	No. 10	No. 11	No. 12	No. 13 Per Cent	No. 14 Colclough	No. 15 Herty	No. 16 Stoughton
C	0.07	0.06	0.06	0.09	0.07	0.06	0.04	0.06
Mn	0.17	0.16	0.10	0.11	0.16	0.22	0.19	0.27
P	0.012	0.012	0.017	0.11	0.048	0.066	0.036	0.035
FeO	10.79	10.61	8.58	7.46	10.90
Fe ₂ O ₃	8.71	8.91	11.10	4.69	5.70	3.91
FeO*	22.57	22.64	16.10	4.68	14.90	15.15	16.16	18.70
SiO ₂	0.0139	16.20	14.69	25.88	19.49	19.19	11.18	18.72	13.66
P ₂ O ₅	0.0167	1.78	1.55	1.47	1.13	3.15	15.01	5.75	5.42
Cr ₂ O ₃	0.0071	0.36	0.34	0.66
TiO ₂	0.0066	0.36	0.34	0.66
V ₂ O ₅	0.0125	1.59	1.71	3.14*	1.12	4.43*	3.24*	5.42	4.49
Al ₂ O ₃	0.0055	2.46	1.84	0.62
Mols Total Acids	0.0100	1.18	1.18	1.78
Mols-FeO _s	0.3143	0.3030	0.4730	0.3726	0.3846	0.3260	0.4065	0.3117
CaO	0.0179	0.3131	0.3144	0.2218	0.2422	0.2071	0.2110	0.2246	0.2600
MnO	42.08	42.28	38.70	45.70	38.08	34.81	34.91	44.21
MgO	0.0139	6.70	6.48	3.93	3.19	6.91	7.26	12.83	8.12
Mols Total Bases	0.0250	6.81	7.57	11.17	8.76	13.73	13.63	6.38	5.76
K	1.0149	1.0369	1.0174	1.0776	1.1199	1.0634	0.9597	1.0469
Mol Fract. Avail. Base	0.310	0.292	0.465	0.346	0.344	0.307	0.424	0.298
Mol Fract. FeO _s	0.2873	0.3160	0.0727	0.2390	0.2440	0.2159	0.1336	0.2940
	0.1907	0.1902	0.1295	0.1432	0.1207	0.1318	0.1411	0.1607

*Total Incidental Oxides: Average Mol Factor 0.0100.

Slag-Steel Data

Data No.	Mol Factors	No. 17 Herty	No. 18 Herty	No. 19	No. 20	No. 21 Per Cent	No. 22	No. 23	No. 24 Coleclough
C	0.08	0.05	0.09	0.05	0.09	0.16	0.06	0.10
Mn	0.05	0.08	0.16	0.14	0.17	0.23	0.10	0.31
P	0.012	0.012	0.016	0.012	0.009	0.009	0.005	0.156
FeO	15.65	17.30	5.88	5.53
Fe ₂ O ₃	8.90	5.10	4.15	4.70
FeO ₂	0.0139	27.67	24.18	11.47	19.12	27.74	17.82	28.50	11.90
SiO ₂	0.0167	15.61	18.07	23.80	19.10	12.65	16.60	13.80	10.10
P ₂ O ₅	0.0071	2.10	2.25	1.65	1.87	1.82	1.78	1.64	15.70
Cr ₂ O ₃	0.0066	0.32
TiO ₂	0.0125	3.78*	0.98*	2.75*	6.49*	6.69*	7.64*	1.47	5.30
V ₂ O ₅	0.0055	1.96
Al ₂ O ₃	0.0100	1.44
Mols Total Acids	0.3128	0.3306	0.4317	0.3972	0.2910	0.3662	0.2902	0.3317
Mols-FeO ₂	0.3841	0.3359	0.1594	0.2658	0.3860	0.2478	0.3961	0.1650
CaO	0.0179	34.04	37.53	48.70	39.50	37.50	43.50	39.60	36.50
MnO	0.0139	5.09	5.28	5.40	7.33	7.09	7.66	5.10	7.50
MgO	0.0250	12.42	12.16	6.20	7.27	6.44	4.93	7.60	13.80
Mols Total Bases	0.9868	1.0505	1.0958	0.9905	0.9208	1.0087	0.9674	1.1020
R	0.317	0.314	0.395	0.400	0.316	0.365	0.300	0.302
Mol Fract. Avail. Base	0.2445	0.2285	0.1570	0.1890	0.2875
Mol Fract. FeO ₂	0.2281	0.1956	0.0939	0.1608	0.2418	0.1522	0.2394	0.1025

*Total Incidental Oxides: Average Mol Factor 0.0100.

Slag-Steel Data

Data No.	Mol Factors	No. 25 Colclough	No. 26 Colclough	No. 27	No. 28	No. 29 Per Cent	No. 30	No. 31	No. 32
C	0.10	0.13	0.16	0.15	0.15	0.15	0.15	0.025
Mn	0.36	0.25	0.22	0.21	0.15	0.15	0.13	0.025
P	0.259	0.030	0.015	0.012	0.011	0.012	0.011	0.004
FeO	4.80	9.30	7.44	10.52	15.29	14.43	15.29
Fe ₂ O ₃	5.00	5.60	5.67	6.95	7.82	7.13	10.10
FeO ₂	0.0139	11.50	17.20	15.08	19.91	24.01	24.08	28.90	55.50
SiO ₂	0.0167	18.00	8.20	18.78	14.41	12.02	12.74	10.85	7.19
P ₂ O ₅	0.0071	12.60	12.80	1.83	1.93	1.73	1.88	1.89	0.15
Cr ₂ O ₃	0.0066	0.28	0.34	0.29	0.25	0.33	4.64
TiO ₂	0.0125	1.70*	4.50*	2.07	1.73	1.38	1.47	1.52
V ₂ O ₅	0.0055	2.46	2.67	2.63	2.21	2.50
Al ₂ O ₃	0.0100	1.20	1.13	0.97	0.88	0.76
Mols Total Acids	0.4075	0.2730	0.3796	0.3041	0.2563	0.2671	0.2371	0.1517
Mols FeO ₂	0.1600	0.2390	0.2095	0.2767	0.3337	0.3343	0.4016	0.7710
CaO	0.0179	41.80	44.40	44.21	44.28	46.58	45.78	43.50	19.80
MnO	0.0139	9.50	7.80	6.72	7.43	5.61	6.02	6.21	4.09
MgO	0.0250	4.90	5.10	8.08	6.80	5.76	5.89	4.61	8.68
Mols Total Bases	0.9865	0.9308	1.0869	1.0658	1.0557	1.0502	0.9800	0.6282
R	0.413	0.293	0.349	0.285	0.243	0.253	0.242	0.242
Mol Fract. Avail. Base
Mol Fract. FeO ₂	0.1030	0.1650	0.1250	0.1680	0.2025	0.2025	0.2480	0.4975

*Total Incidental Oxides: Average Mol Factor 0.0100.

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DISCUSSION

F. G. NORRIS:¹ As I was listening to this paper I felt that we are most unfortunate in not having had a chance to go over the data more carefully in order to prepare a discussion more worthy of Mr. Cook's interesting paper.

Probably one of the things that calls for some comment is this matter of the reaction between carbon and oxygen. We have thought for some time that the carbon and oxygen product was fairly constant, but we knew that there was some other variable that we had not considered. This explanation that Mr. Cook has worked out is an interesting possibility.

As I understand the subject the acid-base ratio that is used in expressing the carbon product is of great importance, in connection with any method of slag control.

One question I would like to ask is—what are we going to do about sulphur? Some grades we hold below 0.030 per cent sulphur and on other grades, we are told by our metallurgical department, we get better results by keeping below 0.025 per cent sulphur. We are meeting these sulphur specifications but we are not doing it easily. We have to give some attention to it. We work lime through the heat in order to lower the sulphur. The data of this paper indicates that this practice is going to increase the iron oxide. If we are working on a basis of slag control, we have two things that look to me to be rather opposed. If we put in too much lime at the end of the heat, we are going to run up the FeO. This practice is used to secure low sulphur. Is it possible to make low sulphur and low FeO on the same heat?

W. J. REAGAN:² I shall not try to discuss in any detail a paper as comprehensive as this one. I have been fortunate in being able to review this paper in its entirety, and I assure you that when you have an opportunity of reading it you will find it extremely interesting and valuable. Lack of even an abstract preprint makes it almost impossible to try to discuss the mass of

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²Assistant Superintendent, Open-Hearth, Edgewater Steel Co.

material presented. It follows along a great many ideas that we have been able to put into practice on a small scale, and such work, in a production shop, covering thousands of heats, shows even more emphatically the practical value of iron oxide control, and the methods used in this type of control are discussed in considerable detail in the paper. It proves again that for a small amount of effort and the expenditure of relatively small sums, the subject of iron oxide control will show financial returns well worth while.

I want to congratulate Mr. Cook on this fine work and certainly will look forward to the time when the paper will be printed in full and hope that some time in the future we may have the opportunity of spending a whole afternoon discussing and reviewing this paper.

C. H. HERTY, JR.:³ I would like to bring up a few points. Mr. Cook has given us limits for carbon, and FeO in slag, and from a great deal of work which we have done lately, I believe those limits are probably high. In other words, we sometimes tap 0.08 and 0.09 per cent carbon steel with as low as 8 and 9 per cent FeO in the slag, which is somewhat lower than Mr. Cook indicates.

One very important point which should certainly be stressed (Mr. Cook should get full credit) is that the intelligent use of sand in the basic open-hearth furnace is important. As Mr. Cook stated, if you use it incorrectly you may get yourself in trouble, but that is a question of practice making perfect. Mr. Cook has shown very definitely that the FeO in the finishing slag is a function of acid to basic oxygen, or the lime-silica ratio, or whatever you wish to call it. In his data he indicated this was a straight line function. If we take a large number of points and average them, that is what we may get, but I would like to point out now that if we take Mr. Cook's paper, or the 300 or 400 heats I have used in checking up on that particular point, we get a considerable spread at any given lime-silica ratio for the per cent FeO. For example, I have in mind one particular point where with a lime-silica ratio of 2.5, we have a variation in FeO in regular operation of from 14 to 28 per cent over a three months period.

The point I am making is that we cannot rely only on this lime-silica ratio to give us the composition of the slag with respect to FeO. There are other factors, largely physical, which control the composition of the slag with respect to FeO when the heat is tapped.

One other point Mr. Cook has shown us is a beautiful way of calculating a burden based on a given charge. If we knew what was going into the furnace, this would be a beautiful operation, but unfortunately on 75 per cent of the heats made we have finished charging before we knew what the hot metal analysis is. Therefore, we have to make a modification of Mr. Cook's general principle in order to burden our furnaces, and that requires other methods of slag control which must be applied after we have the hot metal in the furnace.

L. E. GATZEK:⁴ The readily apparent merit of Mr. Cook's work is self-evident. Not having the advantage of reading his paper before it was presented, I do not as yet possess a complete understanding of its various

³Bethlehem Steel Co., Bethlehem, Pa.

⁴Staff metallurgist, Wisconsin Steel Works, South Chicago, Ill.

ramifications. I therefore, welcome this opportunity of asking the author a question.

In his orderly presentation, Mr. Cook clearly indicated the practical applications of the acid-base ratio for the control of basic open-hearth slag. I would like to know if the same acid-base ratio is applicable in practice on rimmed heats containing approximately 0.10 per cent carbon, and on killed heats?

D. J. DEMOREST:⁵ One thing that has occurred to me in listening to the paper is that there has not been mentioned the role of magnesia in slag and fluxing.

I am wondering about Mr. Cook's discussion with reference to the fact that in the basic slag magnesia is thrown out of solution by the excess lime, and as shown by quenching studies the magnesia precipitates in slag. Not only that, but the magnesia is capable of dissolving in solid solution to a considerable extent ferric oxide and taking it out of solution in slag, and therefore eliminating it from the role of entering into the usual slag equilibria. I suspect that the same thing would be true if magnesia were considered in connection with its ability to desulphurize. Magnesium oxide is not present in the slag as an oxide in solution if there is much excess lime because the lime precipitates the magnesia out of combination and unless we are fooled by what we see in quenched slag, the magnesia is actually precipitated in solid form in the slag, and as these magnesia crystals precipitate out they contain a large amount of ferrite oxide either in solid solution or as a magnesia iron spinel.

Author's Closure

While one section of the paper deals in a general way with sulphur as referred to by Mr. Norris, there are no exact data available. It is indicated, however, that with two per cent P_2O_5 and a lime-silica ratio in excess of 2.3:1, desulphurization occurred for normal operation. Slag oxidations as low as 15 to 16 per cent are possible at 0.08 per cent carbon with this ratio. Sulphur should be eliminated in the blast furnace, not the open-hearth.

Mr. Reagan's remarks are very much appreciated. We are familiar with his own reports upon this subject and hope to have the pleasure of a detailed discussion with him.

Inasmuch as these data have been confined to simultaneous slag and steel samples taken immediately before furnace additions at tapping, the answer to Mr. Gatzek's question is apparent. The practice for rimmed and killed steels up to that point is closely similar with the possible exception of the optimum temperature ranges.

In reply to Professor Demorest's remarks concerning the action of magnesia in open-hearth slags, he may refer to one highly questionable theoretical calculation in the complete report (not included in the presentation) or more sensibly to page 268 of Colclough's description of melting slags (6). This discussion is based on the elimination of phosphorus from the bath and states that "the relation shows that in a melting slag each molecule of phosphoric oxide is associated with four molecules of lime, while each molecule of silica

⁵Professor of Metallurgy, Ohio State University, Columbus, O.

requires two molecules of base, which may be CaO , MnO , MgO , or, to a very small extent, FeO ." While we do not entirely agree with the mineral hypothesis, the evidence suggests that MgO , for want of a better word, "fluxes" SiO_2 at least before dissolving ferric oxide. Calcium oxide may exert a preferential reaction if present in excess but otherwise the magnesia appears to enter into combination. During these experiments it was not possible to persuade any of the open-hearth men to add MgO to the slags. It was largely eliminated in one series of heats, however, by substituting crushed limestone for dolomite in repairing slag lines without causing any remarkable differences in iron oxide control, phosphorus removal or desulphurization.

The first publication that we have seen concerning the use of silicious additions referred to by Dr. Herty appeared in a paper by Colclough before the British Iron and Steel Institute in 1923 where he mentions "the well-known use of sand" in English basic open-hearth practice. It was not described, however, for routine practices. Dr. Herty's criticism of the limits of the possible reduction of iron oxide below 14 per cent for 0.08 per cent residual carbon is probably justified. While lower values had not been observed for the particular operation up to 1933, they may very well be associated with changed conditions such as a more reducing furnace atmosphere for example.

A variation of 14 to 28 per cent in slag oxidation over a three months' period with a constant lime-silica ratio of 2.5 per cent is difficult to reconcile with our observations, even for individual heats if the data cited by Dr. Herty refer to a similar carbon end point and only ordinary variations of P_2O_5 . We are not yet inclined to accept the proposition that "other factors, largely physical, control the composition of the slag with respect to FeO when the heat is tapped" under conditions approaching equilibrium. It would be interesting to examine complete analyses of simultaneous slag and steel samples before additions in relation to this hypothesis. The evidence thus far does not allow definite conclusions toward a general slag oxidation theory based on either physical or chemical principles.

This discussion is not intended as a defense of the lime-silica ratio method, although it permits an excellent measure of control under close supervision with a knowledge of other contributing variables such as P_2O_5 and residual carbon. Acknowledgment of its limitations led to the various studies underlying the burden calculations embodied in the report which it is hoped may contribute to the background for further study of the intriguing possibility of the existence of a simple general formula expressing the gas-slag-steel-temperature relationships for refining. An important discrepancy in the presentation exists in the absence of data from other than one plant, and the lack of direct evidence including wide variations of slag constituents other than CaO and SiO_2 . Our interest in these problems was originally inspired by Dr. Herty's many valuable contributions to the physical chemistry of steel making. It is anticipated that continued co-operative investigation in this important field over the next few years will do much toward reducing melting practices from an art to an applied science.

THE MAGNETIC PROPERTIES OF A SERIES OF BASIC OPEN-HEARTH SLAG SAMPLES

BY B. A. ROGERS AND K. O. STAMM

Abstract

Investigation was made of a series of open-hearth slag samples taken from a single heat of steel. The samples were first pulverized. The powder so obtained was then separated into different sizes by sieving. Selective sizes were then separated magnetically into classes of different magnetic susceptibility. When examined microscopically the most magnetic class was found to be the most interesting. It contained three types of particles: (1) small metal globules, (2) small, thin, curved, metal flakes, (3) particles of slag in which small particles of metal were embedded. Many of the globules were found to contain cavities. Some of the cavities were filled with slag while others were lined with it. The susceptibility of the less magnetic classes was found to vary considerably under heat treatment in vacuo in the vicinity of 600 degrees Cent.

INTRODUCTION

THE intimate relationship between the nature of the slag layer and the quality of the steel produced under it is well recognized, as is evident from the number of investigations that have been conducted on this subject. Studies have been made of slags in the liquid state and also after cooling to the solid state. In both cases the object of the research has usually been to obtain knowledge concerning the conditions at high temperature.

Knowledge of the magnetic properties of slags is desirable for a number of reasons. The oxidizing power of a slag is ordinarily considered to depend upon the state of the iron oxides which it contains. Evidence of the presence of magnetite, calcium ferrite, or other magnetic compounds therefore becomes of considerable interest. Furthermore, there is the important question of the presence of metal in the slag. It has been pointed out that the effect of this distribu-

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A paper presented before the Eighteenth Annual Convention of the American Society for Metals, Cleveland, October 19 to 23, 1936. Of the authors, B. A. Rogers is acting engineer in charge, Iron and Steel Unit, Special Studies Section, Metallurgical Division, U. S. Bureau of Mines, and K. O. Stamm is physical science aid of the same division, Pittsburgh. Manuscript received June 14, 1936.

tion or dispersion of iron within the slag is likely to be a potent factor in the refining action which takes place in an open-hearth furnace. For this reason evidence concerning the nature of this metal-in-slag dispersion is important.

With these ideas in mind, an investigation of the magnetic properties and constituents of open-hearth furnace slags was initiated. The first undertaking and the one which provided the experimental basis of the present paper was the investigation of a series of slag samples taken from a single heat of 0.40 per cent carbon steel. The work has been of an exploratory nature and its purpose has been to point the way to more exactly defined studies rather than to furnish important and definite conclusions upon the nature of slags.

HISTORICAL DISCUSSION

There have been a number of investigations in which the presence of magnetic constituents in furnace slags has been observed. For example, Stead and Ridsdale¹ examined crystals taken from the interior of slowly cooled masses of basic Bessemer slag and found six different types which they could separate out mechanically in sufficient amounts to permit chemical analysis. Of these six types of crystals, two were found to be magnetic. Bainbridge² was able to separate out a gray constituent from slowly cooled basic open-hearth slags which had been powdered. After concentrating by repeated magnetic separation he analyzed the material and found it to contain:

SiO ₂	1.30 per cent	MnO	14.04 per cent
Al ₂ O ₃	1.84 per cent	CaO	7.40 per cent
Fe ₂ O ₃	23.29 per cent	MgO	24.90 per cent
FeO	26.23 per cent	P ₂ O ₅	1.03 per cent

The magnetic constituent which was observed by Ferguson³ had, according to his analysis, 6.36 per cent FeO and 34.10 per cent Fe₂O₃. It is probable that the high proportion of Fe₂O₃ found by these experimenters was caused in part, at least, by the oxidation of FeO during cooling. In his studies of the CaO-Fe₂O₃-SiO₂ system, Sitz⁴ found that it was necessary to quench his slag samples in order to prevent oxidation during cooling.

¹J. E. Stead and C. H. Ridsdale, "Basic Slag: Its Formation, Constitution, and Application with Special Reference to Crystals Found Therein," *Journal, Iron and Steel Institute*, Vol. 30, 1887, p. 222-230.

²F. Bainbridge, "The Effect of Fluorspar Additions on the Phosphates in Basic Slag," *Carnegie Scholarship Memoirs*, Vol. 10, 1920, p. 1-40.

³J. M. Ferguson, "Notes on the Basic Open-Hearth Process," *Journal, West of Scotland Iron and Steel Institute*, Vol. 42, 1934-35, p. 13-20.

Sitz⁴ investigated the change of susceptibility of artificial CaO-Fe₂O₃-SiO₂ slags upon heating. From the temperatures at which sudden changes of susceptibility occurred, he concluded that they contained both magnetite and calcium ferrite.

C. W. Davis began some studies of the magnetic properties of powdered open-hearth slags at the Bureau of Mines Experiment Station in Pittsburgh, but because of the pressure of other work he dropped the investigation at an early stage. He had, however, made two interesting observations:

1. The magnetic susceptibility of slag samples taken during the early stages of a heat of steel was greater than that of samples taken near the finish.

2. The magnetic susceptibility of samples taken at all stages was increased by heating to 625 degrees Cent. (1160 degrees Fahr.) in a neutral (nitrogen) atmosphere. Changes also occurred when the samples were heated to a similar temperature in either hydrogen or in oxygen.

SELECTION AND PREPARATION OF MATERIAL USED IN THIS INVESTIGATION

For the present investigation, which is an outgrowth of the work begun by Davis, it was decided to obtain a series of slag samples taken at intervals from a single open-hearth heat of steel. In carrying out the plan the first sample was removed from the furnace shortly after the lime boil began and the last, just before deoxidizing the metal. The samples were taken with a small spoon and were poured into a mold of the kind employed for making the slag cakes which are used in some plants to follow the progress of a heat.⁵ The mold was about 4 inches in diameter, and the amount of slag was usually sufficient to fill the mold to a depth of about $\frac{1}{2}$ to $\frac{3}{4}$ inch. From the total of fourteen samples taken, seven were selected for examination. The time of taking the samples, the carbon content of the heat at the time they were taken, and the appearance of the samples after cooling are given for these seven samples in Table I.

⁴G. Sitz, "Über das System Kalk-Eisenoxyd-Kieselsäure im Hinblick auf seine Bedeutung für die metallhüttenmännischen Schlacken," *Metall. u. Ers.*, Vol. 29, 1932, p. 209-216, 245-250, 269-276, 298-303, 318-323, 339-346.

⁵Rudolf Back, "Die Schlackenprobe beim Siemens-Martin-Verfahren," *Stahl und Eisen*, Vol. 54, 1934, p. 945-954.

Table 1
Description of Slag Cakes Selected for Magnetic Investigation

Sample No.	Time of Taking	Carbon in Bath, Per Cent	Description of Cake
2	10:20 a.m.	Wrinkled top. Iridescent bottom. Top bulged in three places by gas. Black in color.
4	10:50 a.m.	Top nearly smooth. Shiny bottom, iridescent around edges.
5	11:05 a.m.	Gray furrowed top. Generally dull bottom but with some traces of iridescence around edge.
7	11:40 a.m.	Dull and somewhat furrowed top with several blown-out places. Black and somewhat shiny bottom.
9	12:17 p.m.	0.60	Top generally dull, but with some smooth, shiny patches. Gray bottom, partly smooth, partly rough. (Sample may have started to solidify in the spoon.)
12	1:07 p.m.	0.50	Smooth, black, and generally shiny top but with some smoky areas. Gray and generally dull bottom. Rounded edges.
14	1:32 p.m.	0.38	Smooth, black top but with some grayish regions. Generally rough bottom with some gray spots. Edges much rounded.

NOTES:

1000 pounds of cinder added at 11:05 a.m. just after taking sample No. 5.

75 pounds of sand and 400 pounds of cinder added at 11:25 a.m.

100 pounds of dolomite thrown against the banks in one area between the above additions.

75 pounds of sand added at 12:25 p.m.

200 pounds of cinder added at 12:30 p.m.

Silicon-manganese deoxidizer added at 1:40 p.m.

Heat tapped at 1:50 p.m.

Total time of heat—9 hours and 40 minutes.

A part of each of the seven slag cakes was then crushed for examination according to the following schedule:

Process No.	Treatment
1	Crushed by hand in mortar until largest pieces were about the size of a large pea;
2	Magnetic material, mostly pellets of metal, removed with the hand magnet;
3	Remaining material ground in a Braun disc pulverizer with the plates set at approximately $\frac{1}{8}$ -inch distance;
4	Magnetic material removed with hand magnet and put aside for further examination if desired;
5	Remaining material run through pulverizer with plates adjusted to give the largest particles in the -28 +48 mesh screen size;
6	Ground material separated by sieving into the following screen sizes: -28 +48, -48 +65, -65 +100, -100 +150, -150 +200, -200 +270, -270.

After the material had been separated into fractions of different sizes according to process 6 of the above outline, a magnetic separation of each portion was carried out. This operation was performed by causing the powder to pass through a vibrating tube located in the gap of an electromagnet. The brass tube was sloped at an angle of

about 18 degrees from the horizontal and vibrated longitudinally at a speed of 120 vibrations per second. The gap of the magnet was tapered, with the most intense field at the upper part. When the powder in the vibrating tube reached the region of the magnetic field, the most magnetic particles were attracted to the top of the tube and remained there while the less magnetic passed on out of the tube. The magnetizing current was then cut off and the magnetic portion allowed to fall through the tube into a separate container. By increasing the magnetizing current and passing the residue from the previous operation through the brass tube, it was possible to obtain an additional portion of powder, slightly less magnetic than the material retained in the tube during the first separation. This operation was repeated until six fractions of successively smaller magnetic susceptibility were obtained. In conducting the magnetic separations, an initial sample of 5 grams was taken.

APPARATUS USED IN THE INVESTIGATION

Of the apparatus used in conducting this investigation only that part used in carrying out the measurement of magnetic susceptibility requires detailed description.

The principle involved in measuring the susceptibility of the samples is the familiar one of measuring the mechanical force on an object placed in a magnetic field of nonuniform intensity. The force on a particle located in such a field is

$$f = mXH \frac{dH}{dy}$$

where f is the force in dynes tending to move the particle in the y direction, m is the mass of the particle in grams, X is the mass susceptibility in C.G.S. units, H is the intensity in oersteds of the magnetic field in which the particle is located, and $\frac{dH}{dy}$ is the gradient of the field in oersteds per centimeter.

The magnetic field employed was that existing in the gap of a strong electromagnet. The authors were fortunate in being permitted to use, through the courtesy of S. G. Frantz, the designer, an electromagnet with pole faces which were especially shaped to produce an isodynamic field in the gap. The property of such a field is that the

product $H \frac{dH}{dy}$ is constant at any point in the field. H and its gradient were determined by ballistic measurements at various points in this field. The result of measurements of accuracy sufficient for the purpose in mind showed that the value of this product was

$$H \frac{dH}{dy} = 23.9 \times 10^6$$

under the conditions maintained throughout the investigation.

The force on a substance placed in such a field may be determined simply by attaching it to one arm of a balance, but it was found convenient to use the magnetic balance now to be described. The

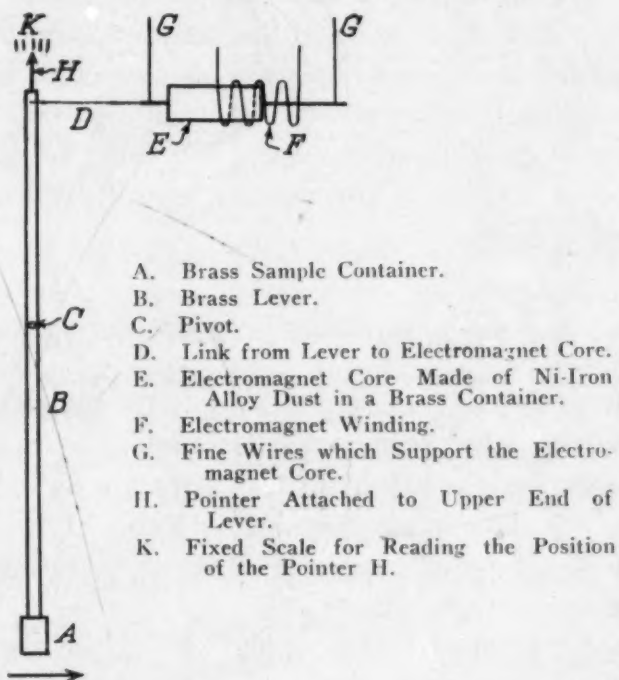


Fig. 1—Sketch of the Elements of the Magnetic Balance Used to Determine Mass Susceptibilities.

use of this balance requires that the Frantz electromagnet should be set with the generatrix of its pole faces in the vertical direction; that is, so that the sample tends to move in a horizontal direction. The magnetic balance consists of a vertical lever pivoted slightly above its center of gravity with the sample container attached to the lower end and the movable core of a small electromagnet linked to the upper end. With current flowing in the winding the movable core is at-

tracted into the electromagnet coil. By calibrating the device it is possible to calculate from the current in the small electromagnet, the mechanical pull, f , necessary to keep the lever in the vertical position when the sample is in the field of the large Frantz magnet. A diagram of the balance is shown in Fig. 1. The arrow shows the direction in which the field intensity increases and hence the direction in which the sample tends to move.

The mass is determined by weighing. X , which is the quantity sought, is, of course, obtained by solving the equation after substituting numerical values for the other symbols.

In carrying out the heat treatments, the samples were placed in a sealed silica tube passing through an ordinary laboratory electric tube furnace. The silica tube was then exhausted with a Hyvac pump and the system tested for leaks before the power was turned on.

For visual observation at low power a binocular microscope with a magnification of approximately 50 diameters was employed. The examinations at higher power were made on polished sections with a Leitz metallographic microscope. For this purpose the powders were mounted in bakelite in the manner frequently used for small metallographic specimens.

DISCUSSION OF DATA

The Magnetic Separation—While the magnetic separation of the powdered slags has been considered under the section on the preparation of samples, the results of this work are of some interest in themselves. The data is summarized in Table II, which shows the percentage of a 5-gram sample held in the vibrating brass tube at different magnetizing currents.

Examination of this table shows that the samples taken early in the heat are composed largely of material which is moderately magnetic. On the other hand, samples taken near the finish of the heat contain a predominant amount of material of relatively low susceptibility. This result confirms the first conclusion reached by Davis. It will also be noticed that there is a tendency for the material in the finer screen sizes to show a higher percentage of the strongly magnetic fractions than is demonstrated by larger sizes of powder from the same slag sample.

It is obvious that the amount of material obtained with magnetizing currents of 0.1 and 0.2 ampere is lower than that actually exist-

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Table II
The Distribution of Powdered Slag Samples into Classes with Different Magnetic Susceptibilities

Sample No.	Screen Size	Per Cent of Sample Retained with Magnetizing Current of					Residual	
		Amperes						
		0.10	0.20	0.50	1.00	2.40		
2	— 48	+ 65	0.42	4.32	17.82	39.62	33.17	4.72
2	— 65	+ 100	0.36	3.40	15.03	40.46	36.32	3.98
2	— 100	+ 150	1.03	2.82	14.80	40.52	35.88	4.58
2	— 150	+ 200	2.88	1.83	11.18	35.44	34.00	13.40
2	— 200	+ 270	4.67	1.48	7.10	40.29	41.20	3.38
2	— 270		4.20	1.40	2.78	61.32	22.06	0.16
4	— 48	+ 65	0.35	3.14	10.45	23.00	52.54	10.61
4	— 100	+ 150	1.25	1.90	10.56	23.20	46.69	16.23
5	— 48	+ 65	1.19	7.34	5.76	4.92	18.21	62.40
5	— 100	+ 150	2.87	4.22	4.96	3.88	13.89	68.29
7	— 48	+ 65	0.25	0.75	1.53	3.24	35.06	59.38
9	— 48	+ 65	0.41	0.36	1.57	5.03	41.80	50.70
12	— 48	+ 65	0.39	0.52	1.77	3.48	27.13	66.47
14	— 48	+ 65	0.25	0.47	2.08	3.25	8.73	85.12
14	— 200	+ 270	3.44	0.55	1.24	1.31	4.44	87.40

ing in the original slag samples because no account has been taken of the portion which was removed with the hand magnet. Magnetic separation of the substance removed in this way indicates that the original samples as treated by process 3 contained from about 2 to 7 per cent of material which was in the 0.1-ampere class and from about 0.2 to 0.5 per cent, which was in the 0.2-ampere class. A large proportion of the 0.1-ampere class of particles obtained with the hand magnet consisted of metal globules too large to go into any of the sizes shown in Table II. Experiments on screening indicated that the fraction in the -48 +65 screen size would have increased the percentages in the 0.1-class by 0.2 to 0.4 per cent. The hand-separated portion, which would have fallen into the 0.2-ampere class of any grain size, was much less than this amount.

Susceptibility of Magnetic Classes—While the susceptibility of the material retained by a definite current in the winding of the separator magnet varied somewhat from sample to sample, the approximate values were always found to be as shown in Table III. The susceptibilities are measured in a field of 10,000 oersteds.

Table III
Approximate Mass Susceptibilities of Slag Powders Separated Out at Different Magnetizing Currents

Magnetizing Current	0.1	0.2	0.5	1.0	2.4
Approximate Susceptibility $\times 10^6$	8000	600	250	140	60

Effect of Heat Treatment—A study was conducted of the effect of heat treatment on $-48 + 65$ screen-size powders of different magnetic classes of samples No. 2 and No. 12. These samples may be considered as representative of the condition of the slag early in the heat and just before deoxidation. All were carried together through a succession of heat treatments in vacuo beginning at 600 degrees Cent. (1110 degrees Fahr.) and their magnetic susceptibility was measured at room temperature after each treatment. In general the treatments were for 3-hour periods and were repeated at the same temperature until the susceptibility appeared to have attained a practically constant value.

The magnetic susceptibility after each treatment is shown in Table IV.

Table IV
The Effect of Heat Treatment in Vacuo of Powdered Slag Samples No. 2 and No. 12

Heat Treatment of Slags Each treatment is in addition to that previously employed	Magnetic Current in Amperes						
	Mass Susceptibility $\times 10^6$ of Four Magnetic Classes of Slag Sample No. 2				Mass Susceptibility $\times 10^6$ of Three Magnetic Classes of Slag Sample No. 12		
	0.2	0.5	1.0	2.4	0.5	1.0	2.4
As taken from open-hearth furnace	620	248	120	64	296	166	56
3 hours at 600° C.	640	315	241	167	472	290	179
3 hours at 600° C.	640	326	240	168	418	263	126
3 hours at 600° C.	460	259	126
3 hours at 700° C.	632	316	223	148	380	161	61
3 hours at 700° C.	349	111	42
10 hours at 700° C.	103	36
3 hours at 800° C.	492	156	88	53	...	*	26
3 hours at 800° C.	447	127	70	46	...	*	27
10 hours at 800° C.	391	93	49	40
3 hours at 900° C.	157	51	33	35
3 hours at 900° C.	132	55	36	40
3 hours at 1000° C.	105	72	56	59	...	*	33

*Sample was put through the heat treatment but not measured because of insensitivity of apparatus at low values of susceptibility with small samples. Only 55 milligrams of this sample were available.

The results given in this table indicate that, for the particular conditions of the experiment, the following generalizations may be made:

1. Treatments at 600 degrees Cent. (1110 degrees Fahr.) increase the magnetic susceptibility up to a certain point. However, an extended treatment at 600 degrees Cent. (1110 degrees Fahr.) appears to lower the susceptibility of a sample taken during the later stages of the heat but to have little effect on one taken early in the heat. These results are confirmed by heat treatments at 700 degrees Cent. (1290 degrees Fahr.).

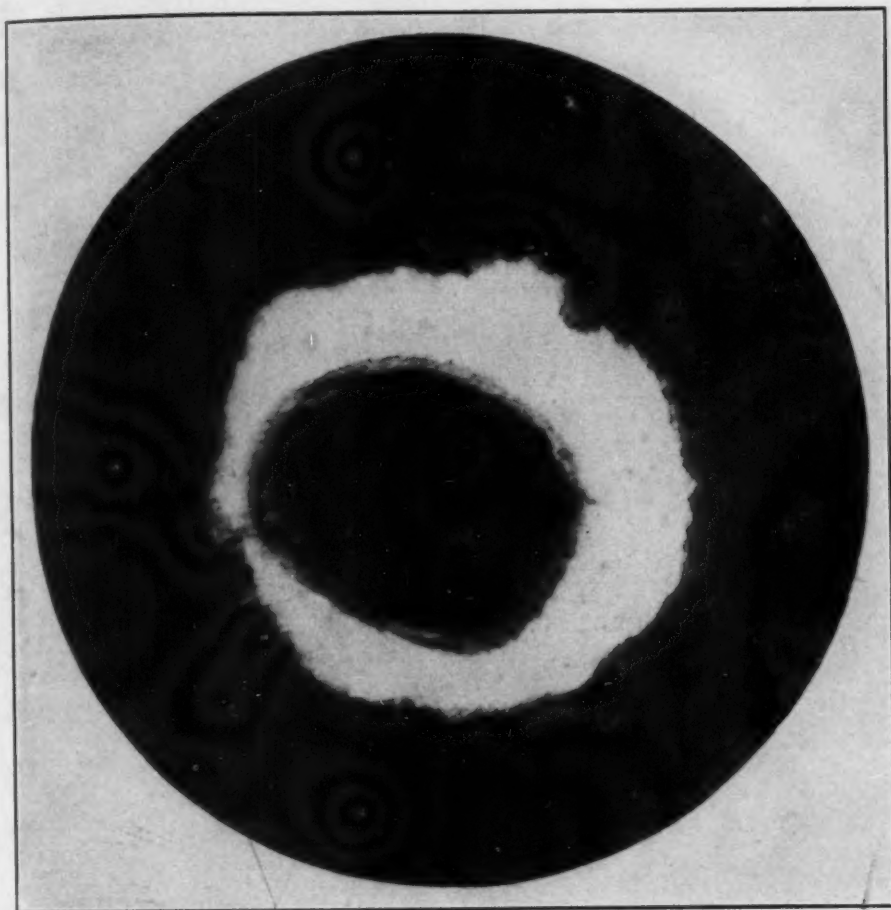


Fig. 2—Section of a Cavity in a Sphere Found in Sample No. 2, Unetched, Mounted in Bakelite. $\times 100$.

2. The more magnetic classes are much less affected by heat treatment at temperatures up to 700 degrees Cent. (1290 degrees Fahr.) than the less magnetic classes.

3. Treatments at high temperature reduce very considerably the susceptibility of the more magnetic classes.

It may be added that treatments at lower temperature indicate that the increase in susceptibility sets in first between 250 and 350 degrees Cent. (480-660 degrees Fahr.) for the No. 2 sample and between 350 and 450 degrees Cent. (660-840 degrees Fahr.) for a sample taken late in the heat.

Microscopic Examination—Under the binocular microscope the powders of all the magnetic classes of any given sample except the 0.1-ampere class appeared quite similar. There were, in fact, only slight differences between samples taken early in the heat compared with those taken in the later stages. The grains of samples taken

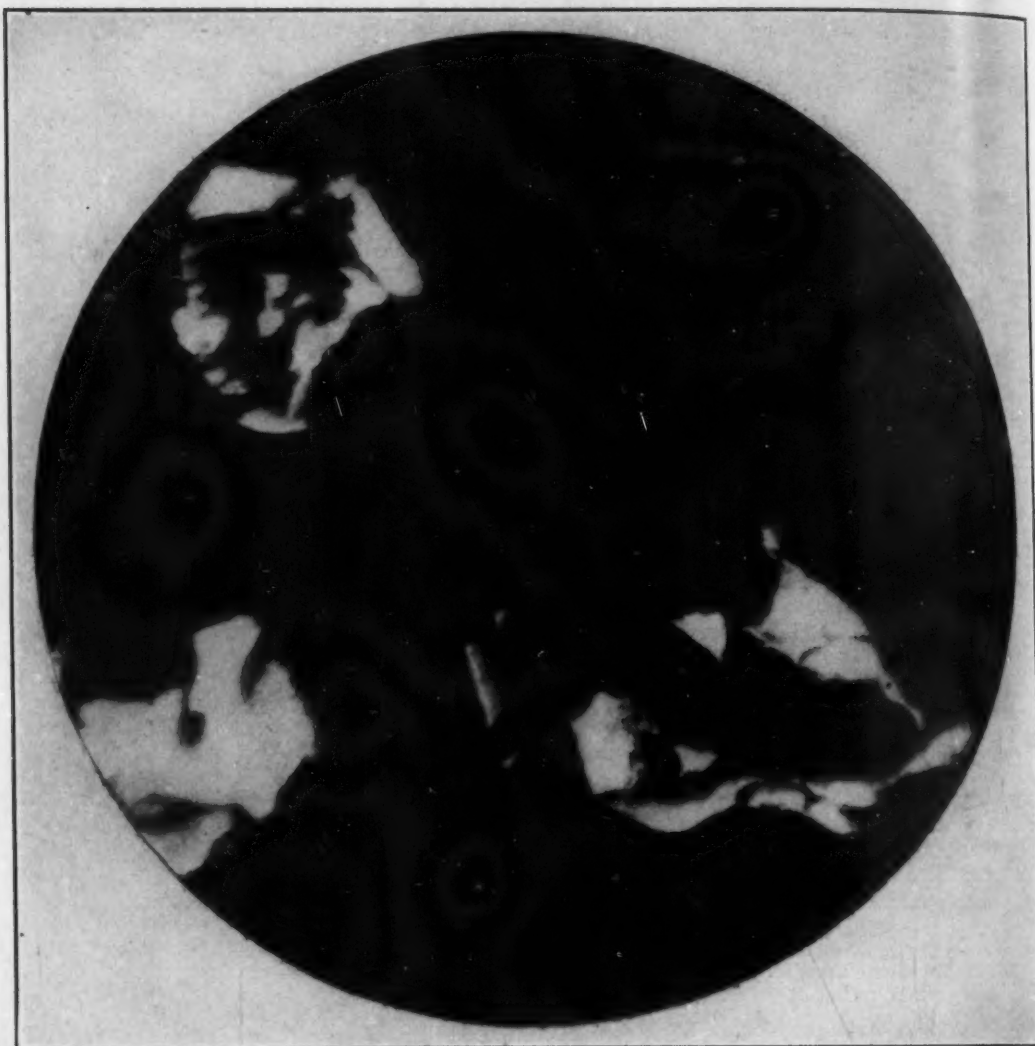


Fig. 3—Section of Flakes from the $-100 +150$ Screen Size Powder of the 0.1-Ampere Magnetic Class of Sample No. 5, Unetched, Mounted in Bakelite. $\times 100$.

early in the heat had somewhat sharper edges, and there were differences in color.

The material which fell into the most magnetic class was of greatest interest. Three different types of particles could be observed:

1. Small balls that appeared to be practically spherical pieces of metal with minute pieces of slag adhering to them,
2. Small curved flakes of metallic appearance,
3. Sharp-cornered grains resembling those found in the other magnetic classes.

All classes of material were found in all samples. The propor-

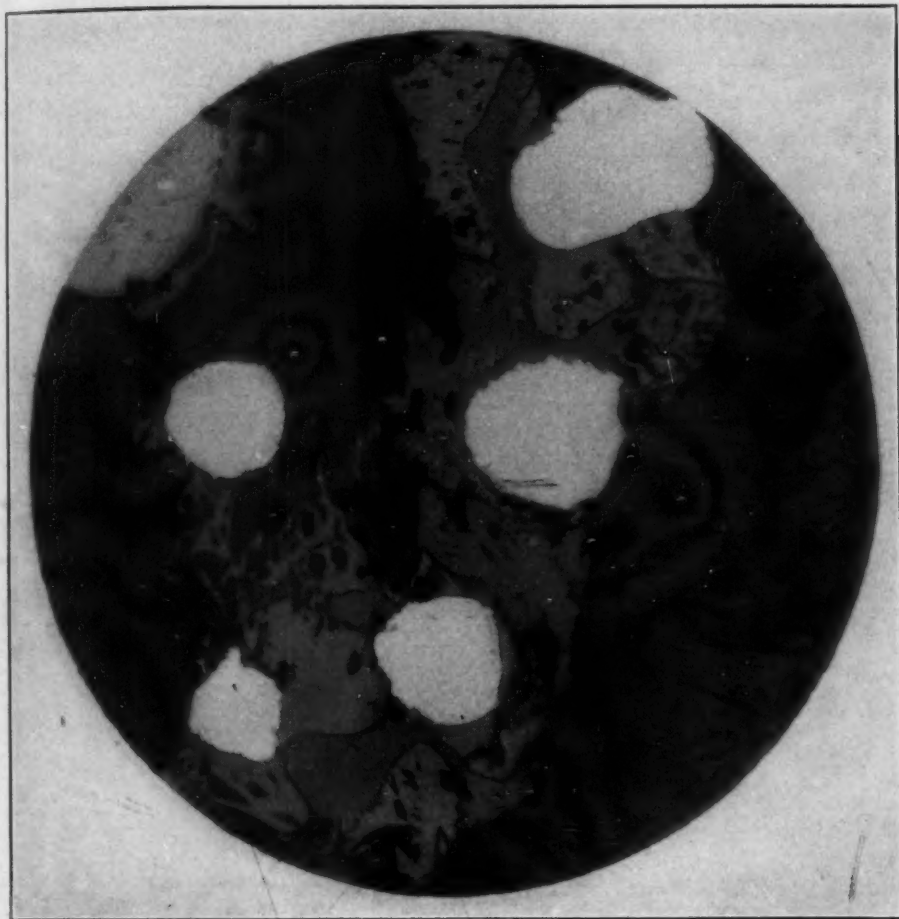


Fig. 4—Section of a Particle of Slag of $-48 + 65$ Screen Size Taken from Sample No. 2; Light Colored Areas Are Metallic Inclusions, Unetched, Mounted in Bakelite. $\times 200$.

tion of these varied somewhat but the distribution may have been accidental.

The presence of metallic spheres in slags used in the manufacture of steel has been noted by a number of writers. Whiteley and Hallimond,⁶ for example, discussed the question at some length and noted that in the early stages of a heat of acid open-hearth steel the carbon content of the spheres was markedly less than that of the bath.

In the present case, the spheres were more frequently found in the coarser fractions and were rarely seen in material which had passed through a 100-mesh screen. The smallest sphere noted under the binocular instrument was approximately 0.005 inch in diameter, but examination of some of the metallic inclusions present in particles

⁶J. H. Whiteley and A. F. Hallimond, "The Acid Hearth and Slag," *Journal, Iron and Steel Institute*, Vol. 99, 1919, p. 199-242.

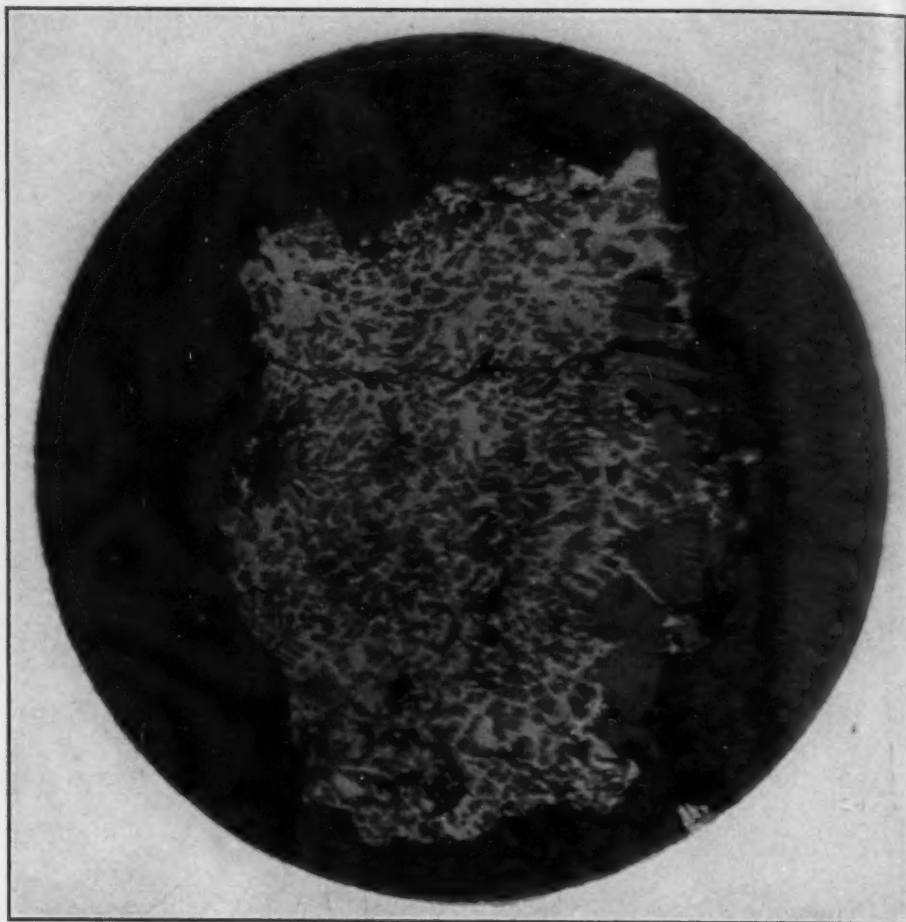


Fig. 5—Section of a Particle of $-48 + 65$ Screen Size Powder of the 0.2-Ampere Magnetic Class of Sample No. 2, Unetched, Mounted in Bakelite. $\times 200$.

of type 3 suggests that smaller spheres do exist, since the cross section of some of these bits of metal was nearly circular. Some of the spheres are hollow and the cavities in all those examined were either filled with slag or lined with it. The appearance of polished sections of these slag-containing spheres is suggestive of the photographs of complex emulsions shown by Seifriz.⁷ It is possible that they originate in a somewhat similar manner. A cavity in a sphere taken from sample No. 2 is shown in Fig. 2.

The authors have not observed any mention in the literature of the curved metallic flakes which are probably the most interesting variety of the highly magnetic particles. That the flakes are practically pure iron was demonstrated by a chemical analysis of flakes picked out from slag sample No. 9, which gave 86.9 per cent total iron and

⁷William Seifriz, "Studies in Emulsions. III—Double Reversal of Oil Emulsions Occasioned by the Same Electrolyte," *Journal, Physical Chemistry*, Vol. 29, 1925, p. 738-749 (Plate I).

86.7 per cent metallic iron. The remaining substance was believed to be composed of particles of slag adhering to the flakes.

At a magnification of 50 diameters, many of the flakes appear little thicker than a sheet of paper and the actual area of those observed was probably anywhere from 10^{-6} to 10^{-2} square inches. Many of them are quite small and it is probably their presence which accounts for the relatively high proportion of 0.1-ampere class material found in the smaller screen sizes. The location of the flakes within the slag material has not yet been determined but they appear to be associated frequently with a type of structure which is very brittle. Unetched flakes of sample No. 5 are shown in Fig. 3.

Fig. 4 shows a particle of sample No. 2 which may be classed as type 3 but which contains a number of pieces of metal. In the picture shown, the metal portions are well rounded but in general almost any shape is likely to be found. The presence of imbedded metal particles of visible proportions does, no doubt, increase the average susceptibility of the type 3 particles. However, not all particles of this type give visible evidence of the presence of metal. A particle consisting largely of magnetite would be drawn into the 0.1-ampere class or the presence of submicroscopic particles of iron might be postulated as an explanation of high susceptibility.

Examination of polished sections of the 0.2-ampere magnetic class particles has not so far revealed the presence of any metallic inclusions. A photomicrograph of such a particle from sample No. 2 is presented in Fig. 5.

For the sake of convenience, the facts brought out during the investigation will now be summarized:

1. Powdered samples of slags cooled in small molds appear to be divisible by magnetic separation into an indefinite number of fractions of successively smaller susceptibility.

2. Slag samples with a low lime-silica ratio appear to have a higher proportion of moderately magnetic material than slags with a higher lime-silica ratio.

3. The effect of heating powdered slag samples in vacuo is to increase or decrease the susceptibility depending upon the temperature. The effect on the fractions of low susceptibility is quite different from that on the portions of high susceptibility.

4. The most magnetic fraction was found to contain three types of particles: metal balls, metal flakes, and slag particles, some of which showed metal inclusions.

Acknowledgment is made to R. S. Dean for suggesting and encouraging the above investigation and to Karl Wentzel in the photomicrograph work and to J. P. Riott for chemical analysis.

DISCUSSION

Written Discussion: By H. J. Sweeney, chief metallurgist, Youngstown Works, Republic Steel Corp.

In reviewing this paper I was impressed with the possibilities offered in this method of slag study. The work performed has been of an exploratory nature yet it proves that the constituents of basic open-hearth slags have varying magnetic properties that can be made use of in several ways. I have two in mind:

1. Rapid magnetic tests on the floor of the open-hearth for control purposes with the view of—
 - (a) Determining the lime silica ratios of slags.
 - (b) Determining the oxidizing properties of slags.
2. Concentrating basic open-hearth slags for charging back into the blast furnace.

The latter use, I believe, offers the more promising view from a commercial standpoint. At the present time it is possible to charge only a relatively small amount of the open-hearth slag produced back through the blast furnace because of desired phosphorus limits in the pig iron. For that reason the material composing the various groups that can be separated magnetically should be carefully examined to determine the possibility of phosphorus segregating in certain groups. In other words, the recovery of iron and manganese from the open-hearth slag by charging in the blast furnace is not so much the concentrating of these materials as it is the segregating and elimination of the phosphorus. With the exception of phosphorus and possibly silica, the other compounds of the basic open-hearth slags are desirable material for charging into the blast furnace.

The possibilities offered along these lines will, of course, be obscure until a careful study is made of the chemical and physical properties of each group that admits of separation magnetically, yet when we realize that there is possibly 150 to 250 pounds of metallics as such per ton of basic open-hearth slag, in addition to the iron and manganese contained as oxides, that could be recovered by pulverizing, the problem begins to have the prospects of commercial possibility.

Authors' Reply

Mr. Sweeney's discussion of the possible uses of magnetic tests of slags is of considerable interest to the authors. The work was undertaken with a view of learning more about the nature of slags and the hope that a method of control of the melting process might be developed. The suggestion that magnetic methods might be employed for concentrating open-hearth slags for charging back into the blast furnace adds further interest.

In the analyses which have been made so far, no effort has been made to observe whether the phosphorus tended to fall into any particular magnetic class. If the phosphorus is distributed without regard to the magnetic susceptibility of the slag which contains it, a study of the effect of different heat treatments might lead to interesting results.

EQUILIBRIUM IN THE REACTION OF HYDROGEN WITH IRON SULPHIDE IN LIQUID IRON AND THE THERMODYNAMICS OF DESULPHURIZATION

BY JOHN CHIPMAN AND TA LI

Abstract

In order to provide a sound basis for the thermodynamic treatment of reactions involving sulphur in liquid steel, an experimental study has been made of the reaction of hydrogen with sulphur in liquid iron forming hydrogen sulphide.

The constancy of the equilibrium ratio at constant temperature is interpreted as evidence that sulphur in liquid iron exists as a sulphide whose molecule contains one atom of sulphur and whose formula may be written FeS. The effect of temperature upon the equilibrium constant within the range 1500-1600 degrees Cent. has been determined.

The free energy of FeS in liquid iron is obtained from the equilibrium measurements and the known free energy of hydrogen sulphide. Thermodynamic properties of other sulphides and oxides are obtained from data in the literature.

The data are applied to the reactions involving sulphur in the open-hearth, and to a study of several possible methods for the desulphurization of steel.

ONE of the ever present problems which the open-hearth operator must face is the control of sulphur in his product. The first essential for the production of a low-sulphur heat is the use of a low-sulphur charge and a low-sulphur fuel. When charge and fuel are kept constant, there may yet be a pronounced variation in the final sulphur content from heat to heat. The removal of sulphur from the bath by the slag, and the limitations with which this removal is beset, are qualitatively fairly well understood in most open-hearth plants. Thus, it is known that the factors which favor sulphur re-

A paper presented before the Eighteenth Annual Convention of the American Society for Metals, Cleveland, October 19 to 23, 1936. This paper is taken from a dissertation submitted by Ta Li in partial fulfillment of the requirements for the degree of Doctor of Science at the University of Michigan. Dr. Li is now Professor of Metallurgy at the Peiyang Engineering College, Tientsin, China. Dr. Chipman was formerly with the University of Michigan, and is now associate director of the Research Laboratories of The American Rolling Mill Company, Middletown, Ohio. Manuscript received June 24, 1936.

moval are a highly basic and very fluid slag, agitation at the slag-metal interface, a high temperature, and, in the basic electric furnace, complete freedom from active oxides. The influence of other variables is less clearly understood, and in spite of the progress that has been made in the chemistry of the open-hearth process, there is no broad general method for estimating quantitatively the desulphurizing power of a slag.

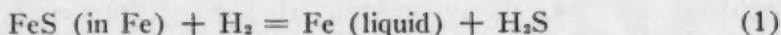
It seems reasonable to anticipate that the application of thermodynamic methods will contribute to our understanding of the behavior of sulphur in the refining of steel. At the same time, it may not be out of order to express the hope that it will lead ultimately to more effective control of sulphur in open-hearth operation.

The thermodynamic data necessary for attacking the problem of the behavior of sulphur can, for convenience, be subdivided in accordance with the three phases in which sulphur occurs. First, there is the gas phase, in which sulphur may occur as H_2S , S_2 , or SO_2 , the other possible compounds being of minor importance. Second, is the slag phase in which the major portion of the sulphur exists as metallic sulphides. Finally, there is the liquid metal in which the sulphur is dissolved, presumably as iron sulphide. The published information on the iron-sulphur system has recently been reviewed by Benedicks and Lofquist (1).¹ They show that iron sulphide is miscible with liquid iron in all proportions. The system is, therefore, very different from the iron-oxygen system, and methods which are applicable to the one may be entirely inapplicable to the other. Nevertheless, it will be shown in a later section of this paper that like oxygen the sulphur in liquid iron exists as a compound whose molecule contains a single atom of sulphur, and whose formula is, therefore, most simply written FeS . The key to the thermodynamic study will be found in this compound, FeS , as it exists in liquid steel. Its properties in this condition cannot be obtained with accuracy by extrapolation of data from lower temperatures, partly because of conflicting data, but more especially because of a complete lack of knowledge as to the ideality or nonideality of the solution. Its most important thermodynamic property, the free energy, can be obtained from an experimental study of its equilibrium with other substances for which this quantity has been accurately established. The properties of hydrogen sulphide are known with a high degree of accuracy, and since it is easily handled, and may be accurately deter-

¹The figures appearing in parentheses refer to the bibliography appended to this paper.



mined, it appeared to be the ideal substance for the purpose. The reaction by which it is formed from iron sulphide in liquid iron is,



The main object of the experiments described in this paper was to determine the condition of equilibrium in this reaction, and thereby to establish the free energy of FeS in liquid iron at steel-making temperatures.

EXPERIMENTAL METHOD

In brief, the principle of the method employed was as follows: An alloy of iron and sulphur is melted in the high frequency induction furnace in a gaseous mixture of hydrogen and hydrogen sulphide. When the sulphur content of the alloy attains a constant value, and when the composition of the gas flowing from the furnace is the same as that flowing into it, equilibrium has been established, and the equilibrium constant can be obtained from the analysis of the gas and of the metal.

Furnace—The induction furnace is shown in Fig. 1. The crucible N holds 50 to 80 grams of metal. It is supported by the silica tube M, and the pyrex tube L. The silica tube A, about two inches outside diameter, is fitted with water-cooled, brass ends. The lower crucible K is used to catch any metal that is dropped by failure of the melting crucible. The gas stream enters at the top through E and passes out through J. In order to avoid any errors occasioned by thermal diffusion such as those observed in analogous experiments with hydrogen and steam (2), the entering gas was preheated by the molybdenum filaments F. These filaments were electrically heated to approximately the temperature of the metal. They were not corroded by the gaseous mixture, although they became rather brittle after repeated use. It was shown by blank runs, in

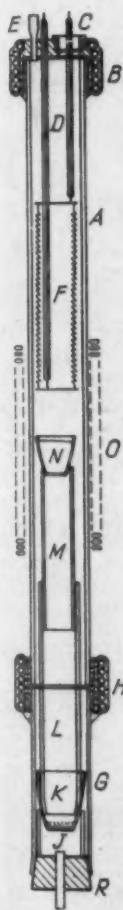


Fig. 1—Induction Furnace. N—Melting Crucible. O—Induction Coil. A—Silica Tube. E—Inlet. J—Outlet. F—Preheating Filament.

which no iron was charged, that the heated filaments did not affect the composition of the gas.

Temperature Measurements—Temperatures were measured by sighting an optical pyrometer of the disappearing filament type through the pyrex window C. This pyrometer had been previously calibrated, and was occasionally rechecked against the melting point of electrolytic iron in the crucible N. The melting point of this iron was taken as 1530 degrees Cent. (2785 degrees Fahr.).

Gas Mixture—Preliminary calculation showed that a gas mixture containing about 1000 times as much hydrogen as hydrogen sulphide should be in equilibrium with metal containing a few tenths of a per cent sulphur. Gas mixtures were prepared under pressure in a steel cylinder which previously had been used for hydrogen. A manifold system fitted with valves and gages was used to connect this cylinder to a small cylinder of hydrogen sulphide, a full cylinder of hydrogen, and a vacuum pump. The cylinder was first evacuated, then hydrogen sulphide was admitted up to any desired pressure, say 0.3 atmosphere as measured on a mercury manometer. Hydrogen was then added to bring the total pressure up to 60 or 70 atmospheres. After standing for several days, during which the cylinder was occasionally inverted, the mixture became very uniform. When the cylinder was first used for this purpose, its walls absorbed a large amount of hydrogen sulphide, resulting in a much lower concentration than was desired. However, after several fillings, a state of saturation was attained, and no further trouble was encountered. The analysis of the mixture was always checked before and after using.

Iron-Sulphur Alloy—After a few preliminary runs in which electrolytic iron was used, it was found convenient to use an alloy of iron and sulphur as the starting material. This alloy was prepared in small batches by melting electrolytic iron in a magnesia crucible in vacuum and adding iron sulphide to the melt. Commercial iron sulphide was used in preparing low-sulphur alloys, but for the higher sulphur contents, a synthetic material, formed by heating flowers of sulphur with electrolytic iron filings, was employed. In several runs the residues of ingots from previous experiments, after sampling for analysis, were employed. The use of iron-sulphur alloys, rather than pure iron, as the starting material, decreased the time required for reaching equilibrium, and also permitted the equilibrium state to be approached from both sides.

Methods of Analysis—The evolution method, with some modifications to promote accuracy, was adopted for the analysis of the alloys and the gaseous mixtures. For sulphur in iron, the sample was first dissolved in dilute hydrochloric acid, and the evolved gas was passed through an ammoniacal solution of cadmium chloride contained in a ten-bulb absorber. The solution flask and absorber were swept out with tank hydrogen before and after solution of the sample. The solution containing the precipitated cadmium sulphide was acidified and allowed to react with an excess of standard potassium iodate solution. The excess iodine was then titrated with standard sodium thiosulphate.

For the gaseous mixture, the gas was drawn through the same absorber, and its content of hydrogen sulphide was determined in the same way. The hydrogen left after absorption was collected over dilute acid, and its volume, after correcting for aqueous tension, was reduced to standard conditions. The molal ratio of H_2S to H_2 was then readily computed. The use of the same method of analysis for the gas and the alloy should virtually nullify any systematic errors in the analytical work.

Sampling—The amount of sample used in the evolution method, should not produce, in the absorbing solution, an amount of cadmium sulphide (CdS) that will require more than 20 cc. of iodate solution. Hence for a sample containing about 1 per cent sulphur, a 0.5 gram sample is a suitable amount to be used in each analysis. For 0.5 per cent sulphur, not more than 2 grams should be used. For sulphur below 0.1 per cent, 5 grams may be used. Therefore, it is evident that special precautions must be taken in order to obtain a representative sample, especially when a very small amount is to be used.

Iron with FeS inclusions is far more brittle than the iron itself. When such a sample is made into filings by drilling, turning, or sawing, the fine particles produced contain more FeS than the coarser ones. For example, the melt from Run 51 was sawed into several pieces by running the saw vertically through the center of the melt. Five analyses were made from these saw filings, the results of which were: 0.667, 0.669, 0.668, 0.640, and 0.667 per cent sulphur. The value adopted was 0.668 per cent sulphur. The remainder of the saw filings was sifted on a 60-mesh sieve. The part retained on the sieve gave an analysis of 0.631 per cent sulphur, while the part which passed through gave 0.715 per cent sulphur.

FeS inclusions may not be distributed uniformly throughout the iron. A number of samples have been polished and examined under the microscope. For a sound melt, or a sample with a single hollow space (pipe) in the middle, the grain size of the iron was uniform, and the FeS which filled out the grain boundaries was distributed uniformly throughout the sample, as shown in Fig. 2. But for a highly porous melt, as those usually obtained from the runs with quartz crucibles, the distribution of FeS was not uniform. The FeS was usually concentrated at the end of each blow hole. Since the blow holes pointed toward the center of the melt, there usually resulted a higher per cent of sulphur in the center than at the edges. In a melt containing sulphur below 0.1 per cent, the FeS existed as elongated globulous forms, and was not distributed uniformly (Fig. 3), even when the melt itself was not very hollow or porous. The following three analyses illustrate very well this segregation of FeS when the sample is porous or when the per cent of sulphur is low:

Run 50—Melt, hollow and porous.

	Per Cent Sulphur
Portion sawed off horizontally at the center	0.618
Portion sawed off vertically at the edge	0.473
Mean values from several analyses of lathe turnings	0.520

Run 55—Melt, hollow and porous. Half of the melt was turned horizontally into three portions.

	Grams	Per Cent Sulphur
Filings from the top	5.0	0.096
Filings from the middle	5.0	0.101
Filings from the bottom	4.0	0.094
Weighted average		0.097

Run 57—Melt, hollow. Half of the melt was lathed vertically into three portions.

	Grams	Per Cent Sulphur
Filings from the outer portion	10.762	0.0934
Filings from the intermediate portion	9.362	0.1033
Filings from the center portion	9.362	0.1033
Weighted average		0.101

Taking these precautions into consideration, most of the melts were sampled by turning them out vertically on a lathe, with a sharp tool, into uniform filings. These were received on a piece of paper spread under the tool, until half of the melt had been consumed. The

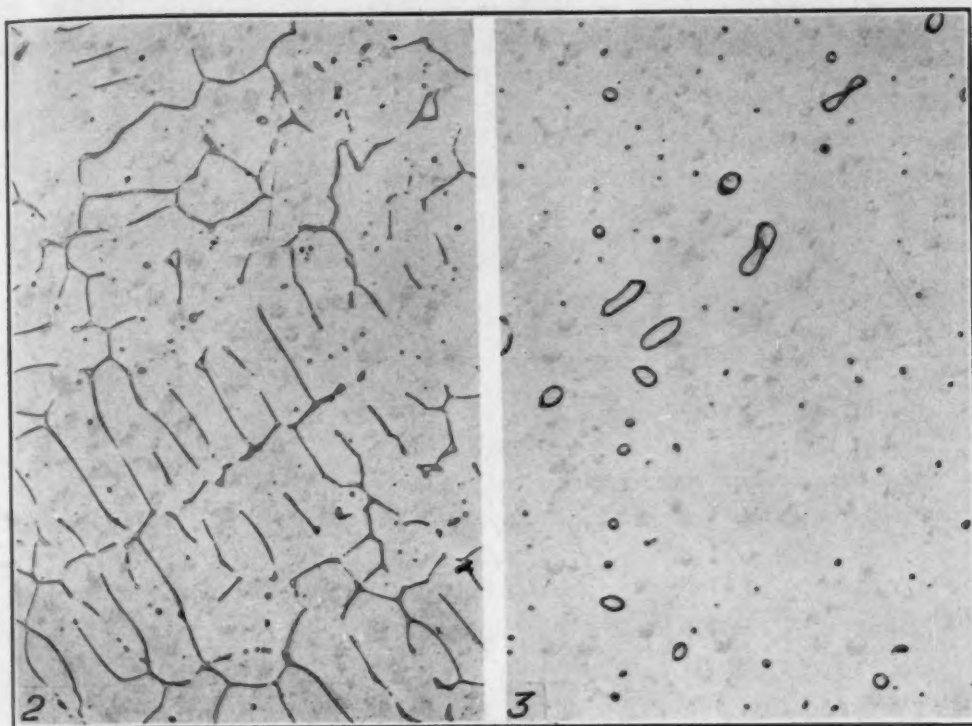


Fig. 2—Iron Sulphide Inclusions in Heat 22. 0.976 Per Cent Sulphur. $\times 100$.
Fig. 3—Iron Sulphide Inclusions in Heat 58. 0.0925 Per Cent Sulphur. $\times 500$.

filings were then mixed thoroughly and the necessary amount weighed out for analysis. If two or three analyses did not give check results, then the determinations were repeated. In many melts from the runs using quartz crucibles, all the filings had to be analyzed, and the weighted average was taken to represent the per cent sulphur in the melt. For a sound sample or a sample with a single pipe, it was usually sawed vertically into halves, and the filings recovered. All the filings which amounted to only 1 to 2 grams were analyzed.

EQUILIBRIUM DETERMINATIONS

The method of carrying out a determination may be briefly described as follows: 50 to 70 grams of the sample was weighed out into the crucible and placed in the furnace. The gas mixture was passed through the furnace for 15 minutes or more, and the power was turned on. After the sample had melted the power input was reduced so that a slow solidification occurred during which the temperature was observed. In the case of the electrolytic iron melts this observation constituted a valuable check on the calibration of

Table I
Preliminary Runs With MgO Crucibles

Run	Duration of Run in Hrs.	Temperature in °C.	Rate of Gas in CC./Min.	$\frac{\text{H}_2\text{S}}{\text{H}_2} \times 10^3$ Entering	% S in Iron	$\frac{\text{Ratio H}_2\text{S}}{\text{H}_2 \times \% \text{ S}} \times 10^3$
9	0.5	1600	400	4.38	0.062	72.9
8	1.0	1600	430	4.66	0.184	25.3
3	1.3	1600	500	1.34	0.051	26.3
4	1.4	1605	500	5.02	0.204	24.6
12	3.0	1600	450	3.61	0.284	12.7
13*	2.0	1600	400	3.61	0.175	20.6
6	1.0	1558	500	4.97	0.124	40.1
10	2.0	1558	500	4.44	0.315	14.1
11	3.9	1558	500	2.84	0.233	12.2
14	5.0	1558	400	4.24	0.447	9.5
5	1.0	1667	500	4.71	0.130	36.2
7	1.3	1759	400	4.97	0.145	34.2

*Preheating filament was not heated up.

the pyrometer. During the melting period, the inlet gas was analyzed. The melt was then brought to the desired temperature and the gas stream to the desired rate of flow. These and the filament temperature were adjusted every five or ten minutes during the run. The outlet gas from the furnace was analyzed every 20 to 30 minutes.

When the time of the run was finished, the power was stopped suddenly and the solidification occurred within a few seconds. The ingot was cooled in the furnace to room temperature, then removed and sampled for analysis.

Preliminary Runs—Time to Reach Equilibrium

Table I gives the results of a set of preliminary runs using magnesia crucibles, starting with pure iron, at a rate of gas kept at about 500 cubic centimeters per minute, and the composition of gas from 3 to 5 volumes of H_2S in 1000 volumes of H_2 . The varying factors that can be studied are the time of run, the temperature of run and the preheating of the gas.

Fig. 4 shows the increase of sulphur in iron with the time of run. Only those runs with higher gas ratios are plotted. Runs 3 and 11, in which the gas has a low ratio, and Run 13, in which the gas is not preheated, are not shown. Since the gas composition and the gas rate were not kept strictly constant, and since it will subsequently be shown that the magnesia crucible itself will absorb some H_2S from the gas, this plot should not be taken to represent the phenomena with any exactness. But qualitatively, this plot, together with Table

I, and observations made during these experiments, does indicate the following facts:

1. There is no evidence of any kind as to the deposition of liquid or solid sulphur in the cold part of the furnace. This confirms preliminary calculation that the gas mixture passing through the furnace should not be decomposed.

2. There is no apparent reaction between the crucible and the FeS or Fe in the melt, for the crucibles after the run al-

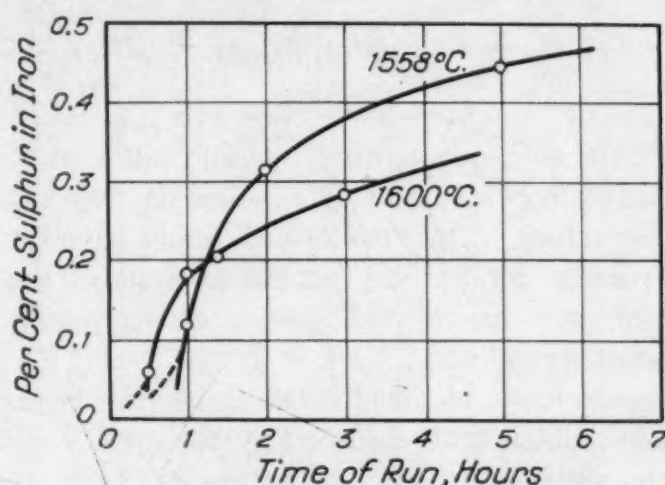


Fig. 4—Increase in Sulphur in Iron with Time of Run.

ways give a clean and white inside surface where it has been in contact with the liquid melt during the run (see Fig. 5).

3. The preheating of the gas mixture has a decided effect on the amount of sulphur absorbed by the iron in such a manner that the lower the temperature to which the gas is preheated, the lower the amount of sulphur which will be absorbed by the iron.

4. The limiting amount of sulphur in iron absorbed from a given gas mixture increases as the temperature decreases.

5. The final and the most important fact is, that, from the shape of the curves plotted, the time for reaching the final equilibrium state would be exceedingly long. For this reason, it was not attempted to reach the equilibrium beginning with pure iron.

Runs with Magnesia Crucibles—From the results of the preliminary runs, it is seen that when starting with pure iron, the time for reaching the final equilibrium is exceedingly long. The equi-

librium can be reached from the low sulphur side more quickly, and just as surely, by starting with an iron-sulphur alloy containing somewhat less than the equilibrium amount of sulphur. It can also be reached from the high sulphur side by beginning with a slightly higher sulphur content.

Table II gives the results of a series of runs using magnesia crucibles, with an initial amount of sulphur in the melt, and a higher gas rate. The first four runs, namely, 15, 16, 17 and 18, give the

limits within which the equilibrium constant
$$K' = \frac{(H_2S)}{(H_2) \times (\% S)}$$

should lie. All the subsequent runs, especially those at 1558 degrees Cent., give fairly close values of K' , indicating that equilibrium is reached at these values. The final results would have been obtained at this stage, were it not for the fact the analysis of the outlet gas near the end of each run always gave a constant value which is lower than that of the inlet gas.

Attempts were made to find the causes of this decrease of H_2S in the gas. It should not be absorbed by the melt, for if the melt is still absorbing sulphur, the H_2S in the gas will keep on decreasing instead of remaining constant; moreover, in most of the runs, the sulphur in the iron actually decreases. No evidence has ever been observed for the FeS going into the walls of the crucible, or for any H_2S being decomposed. The blank test for the furnace shows still further that no H_2S has been decomposed or absorbed by the molybdenum filament. A solution was finally reached from the analysis of the crucible wall.

The crucible, after using, was broken into chips. Each chip was ground on an alundum wheel so as to remove a layer of oxides from both the inside and outside surfaces. The part left, which was perfectly clean and white, was then crushed, powdered, and analyzed for sulphur in the same way as the analysis for sulphur in the melts. According to this method, the crucible from Run 25 gave 0.37 per cent sulphur, and from Run 26, 0.34 per cent sulphur. The solution left in the generating flask in which the powder was dissolved was perfectly colorless, and contained no significant amount of iron. The sulphur in the crucible must be mainly, if not entirely, a sulphide of magnesium or possibly hydrogen sulphide adsorbed by the crucible wall. The formation of magnesium sulphide, by reaction of hydro-

Table II
Results of Runs With Magnesia Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run		(H ₂ S/H ₂) × 10 ³		H ₂ S × 10 ³	
					Condition	% S	Entering	Leaving	Entering	Leaving
15	2	400	1558	0.667	Sound	0.740	4.2		5.67	
16	2	700	1558	0.522	Sound	0.452	1.54		3.41	
17	3	400	1558	0.6	Sound	0.350	0.709		2.02	
18	3	450*	1558	0.1	Sound	0.079	0.215		2.72	
19	4.5	450	1558	1.203	Sound	1.13	5.00	3.55	4.42	3.14
20	2	750	1558	1.08	Sound	1.04	4.72	3.38	4.54	3.26
21	2	750	1558	1.04	Hollow	0.992	4.64	3.30	4.68	3.32
22	2	750	1558	0.992	Sound	0.976	4.38	3.15	4.49	3.23
25	2	750	1600	1.13	Hollow	0.900	3.60	3.11	4.00	3.46
26	2	750	1600	0.900	Pipe	0.780	3.64	2.73	4.67	3.50
23	2	750	1723	0.886	Hollow	0.704	4.16	2.89	5.91	4.11
24	2	750	1723	0.704	Hollow	0.679	4.16	2.89	6.13	4.26
32b	2.3	1000	1507	0.8	Hollow	0.816	3.11	2.75	3.81	3.37

b = Made with beryllium oxide crucible.

gen sulphide with magnesia at high temperature, is thermodynamically possible when, as in the present experiments, the gas is entirely free of water vapor.

A beryllium oxide crucible was used for Run 32. The result was the same as for magnesia crucibles, the crucible wall contained 0.36 per cent sulphur. Obviously neither magnesia nor beryllia can be depended upon for accurate results in the study of this reaction.

Runs with Porcelain Crucibles—Since basic oxide crucibles have been found to be decidedly reactive with H_2S in the gas, and cause great uncertainty for the value of the equilibrium constant, crucibles which are more acidic in nature, and, at the same time resistant to high temperature, should be used. Porcelain satisfies both of these requirements. Naturally crucibles made of porcelain or sillimanite were the next alternatives to be tried.

Table III gives the results of runs with porcelain crucibles. The equilibrium constants obtained in this case are entirely different from those obtained with magnesia crucibles, because, in addition to the lowering of H_2S in the gas, there is a reaction of the melt with the crucible (see Fig. 5). The lowering of the H_2S content in the gas is not appreciable at lower temperatures, but increases as the temperature increases; the total amount lowered is much smaller than that with magnesia crucible runs. The attack on the crucible by the melt increases with the temperature and time of run. The melt turns the crucible black and dissolves it. For example, the lower part of the crucible from Run 29, which had been heated for 6 hours, left only a very thin black crust, which barely held the melt in position. Since the porcelain is made from aluminum silicate, it is probable that the Al_2O_3 in the crucibles causes the lowering of H_2S in the gas and the reaction of the crucible with the melt.

Runs with Silica Crucibles—Since runs with magnesia crucibles gave uncertain results, and those with porcelain crucibles failed to verify them, the next type of crucibles which have decidedly no action with the H_2S in the gas, would be those made of silica. This material has a melting point of about 1700 degrees Cent. (3100 degrees Fahr.). In a chemical laboratory it is not used at a temperature higher than 1200 degrees Cent., because above this temperature the silica devitrifies and undergoes a great decrease in strength. Whether it would be serviceable for this purpose or not, could be determined only by trying it out.

Silica crucibles softened at temperatures higher than 1530 de-

Table III
Results of Runs With Porcelain Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run		$(H_2S/H_2) \times 10^3$		$\frac{H_2S}{H_2} \times 10^3$	
					Condition	% S	Entering	Leaving	Entering	Leaving
27	2	750	1579	0.7	Hollow	0.746	3.50	3.09	4.69	4.14
29	6	1000	1579	0.00	Hollow	0.597	3.26	2.71	5.45	4.53
28c	2	1000	1584	1.145	Sound	0.954	3.56	3.56	3.73	3.73
43d	2	800	1584	1.25	Hollow	1.22	4.85	4.55	3.98	3.73
31	2	1000	1513	1.07	Hollow	1.002	3.15	3.15	3.14	3.14
33	2.5	750	1513	1.002	Hollow	0.925	2.95	2.95	3.19	3.19
46e	2	1000	1546	1.+	Hollow	1.290	4.88	4.46	3.78	3.46

c = Melt contained a few pieces of quartz chips.

d = With unglazed porcelain crucible.

e = With unglazed sillimanite crucible.

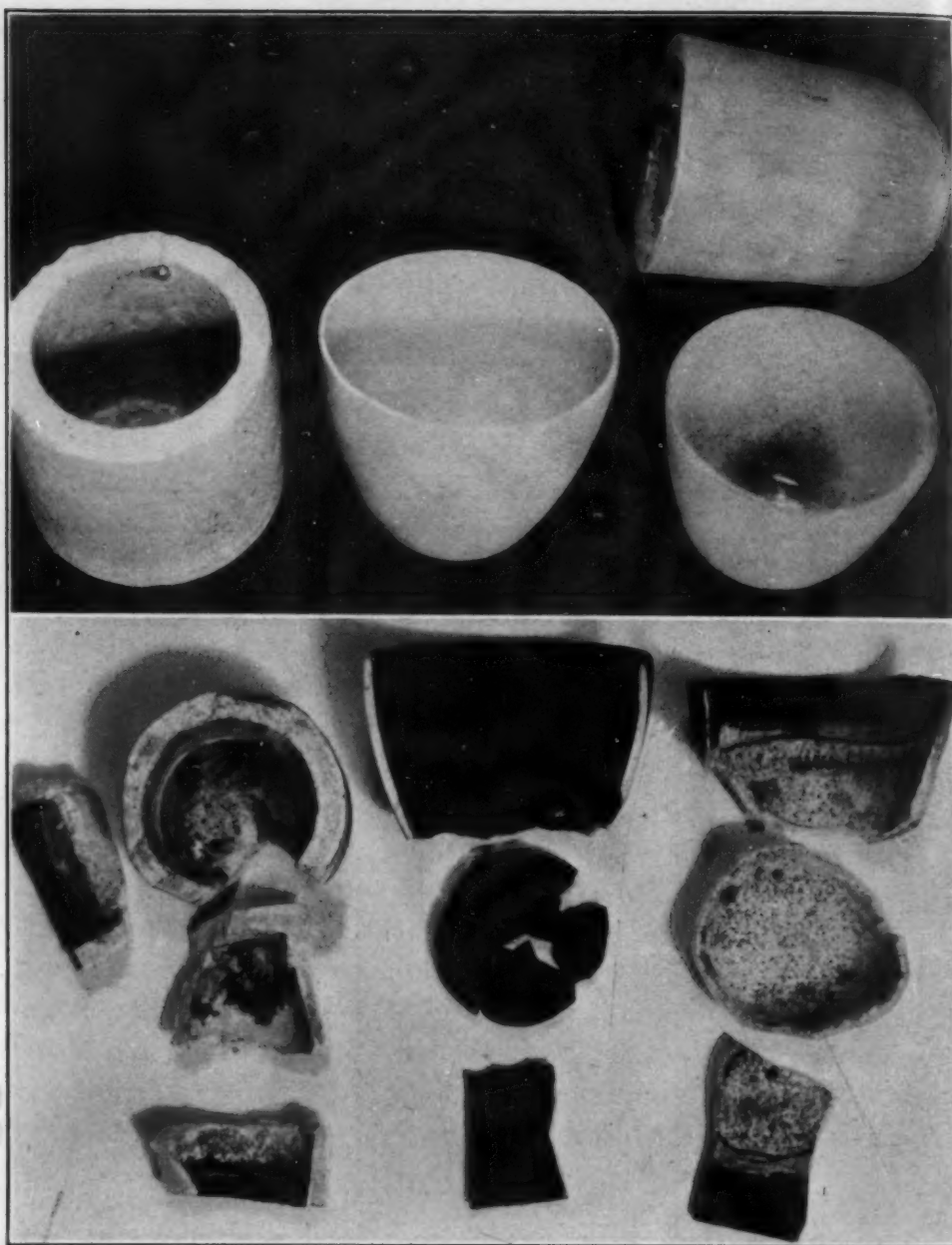


Fig. 5—Crucibles Before and After Run, and Typical Melts Obtained. The Photographs are Arranged to Show at the Left—Magnesia Crucibles, Center—Porcelain, and Right—Silica Crucibles, and Respective Melts.

grees Cent., and occasionally yielded, causing the iron to flow out. Although two runs have been made at 1600 degrees Cent., attempts to run at temperatures higher than this were entirely unsuccessful. At these higher temperatures, 10 to 20 minutes heating made the crucible soft and no longer strong enough to hold the molten iron in position.

Table IV gives the results of runs with silica crucibles. It is seen that the inlet and outlet gases give practically the same analysis. The crucible from each run, although devitrified badly, was clean and white (Fig. 5), showing that it had absorbed nothing from the melt.

The rate of gas used in this series of runs was from 750 to 1050

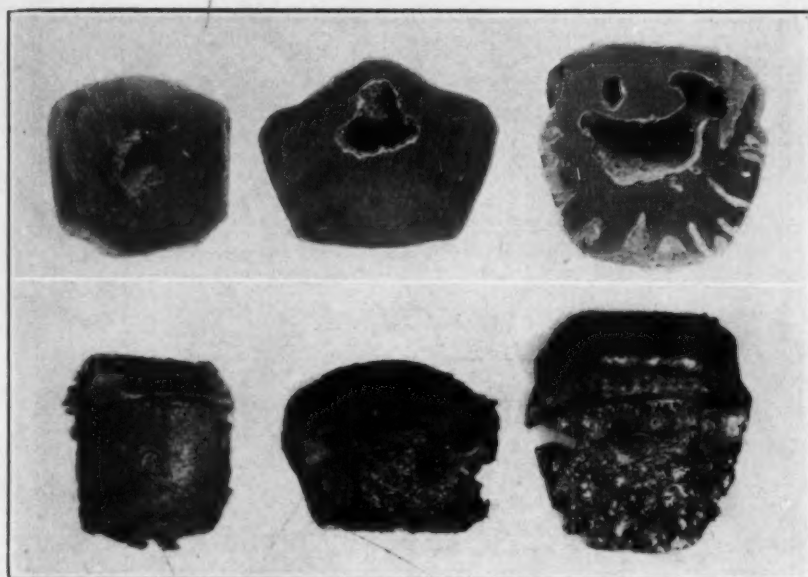


Fig. 5b—Typical Melts from Crucibles in Fig. 5.

cubic centimeters per minute. No effect on the equilibrium constant has been observed by changing the rate from 750 to 1050. An attempt has been made in Run 47 to use a gas rate of 1350 cubic centimeters per minute. At this rate the gas carried with it the sublimed amorphous silica which finally clogged the stop-cock at the outlet end, and stopped the passage of the gas entirely.

Due to the sublimation of silica, a great deal of black amorphous substance collected on the top of the crucible and on the furnace wall. This substance can be decolorized easily by immersing it in HCl, but the main bulk of the substance remained undissolved. This substance, then, must be mainly silica (possibly with some elementary silicon) colored black by iron and FeS which evaporated from the melt and finally condensed with this silica.

Since silica is slowly reduced by hydrogen at high temperatures, it is to be expected that some silicon would be absorbed by the melt. Several melts were analyzed for silica with the following results. Heat No. 52 contained 0.41 per cent; No. 49, 0.81 per cent; and No. 45, 0.86 per cent silicon. The exact effect of this silicon upon the

Table IV
Results of Runs With Silica Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run		$(H_2S/H_2) \times 10^3$		$\frac{H_2S}{H_2 \times \% S} \times 10^3$	
					Condition	% S	Entering	Leaving	Leaving	
34	2.5	750	1513	0.816	Hollow	0.774	2.90	2.90	3.75	
48	2.2	1050	1535	0.00		0.227	2.11	1.35	4.88	
50	2	1050	1535	0.47	Hollow	0.520	2.11	2.08	4.00	
36	2	1050	1535	0.50	Hollow	0.609	2.50	2.45	4.03	
52	2	1050	1535	0.65	Hol. & Por.	0.618	2.10	2.20	3.56	
49	2	1050	1535	0.57	Hol. & Por.	0.541	2.11	2.20	4.07	
51*	2	1100	1535	0.67	Hollow	0.668	2.10	2.21	3.31	
39	2.3	950	1535	1.2	Sound	1.22	4.93	4.99	4.08	
53	2	1050	1546	0.46	Hol. & Por.	0.490	2.10	2.05	4.18	
47	2.1	1350	1546	1.29	Sound	0.983	4.53	4.53	4.61	
56*	2	1050	1558	0.1	Hollow	0.0733	0.42	0.37	5.05	
55	2.5	1050	1558	0.15	Hol. & Por.	0.0970	0.40	0.40	4.13	
54*	2	1050	1558	0.51	Hol. & Por.	0.568	2.11	2.12	3.73	
35	2.4	1050	1558	0.8	Sound	0.639	2.74	2.74	4.29	
58	2	550	1589	0.1	Porous	0.0925	0.40	0.41	4.44	
57	2	550	1589	0.11	Hollow	0.101	0.40	0.41	4.06	
45	2	1070	1589	1.0	Sound	1.03	4.88	4.76	4.62	
44	1.5	850	1589	1.22		^a	4.85	4.78	3.83	
41	2	850	1584	1.3	Hollow	1.25	4.74	4.90	4.91	
37	1.7	750	1600	1.2	Sound	0.998	5.00	5.08	4.00	
38	2.8	800	1600	1.4	Sound	1.27	5.00	5.08		
42	0.8	930	1640	1.3		^a	4.93	4.93		

*With no preheating of gas.
a = Crucible broken during run.

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equilibrium determination was not ascertained, but it seems altogether unlikely that it should be appreciable. As a matter of interest, the oxygen content of two melts was determined by vacuum fusion. No. 53 contained 0.006 per cent, and No. 57, 0.009 per cent oxygen. The porosity observed in nearly all melts made in silica crucibles is unquestionably due to evolution of hydrogen on solidification.

The main source of error in this series of experiments comes

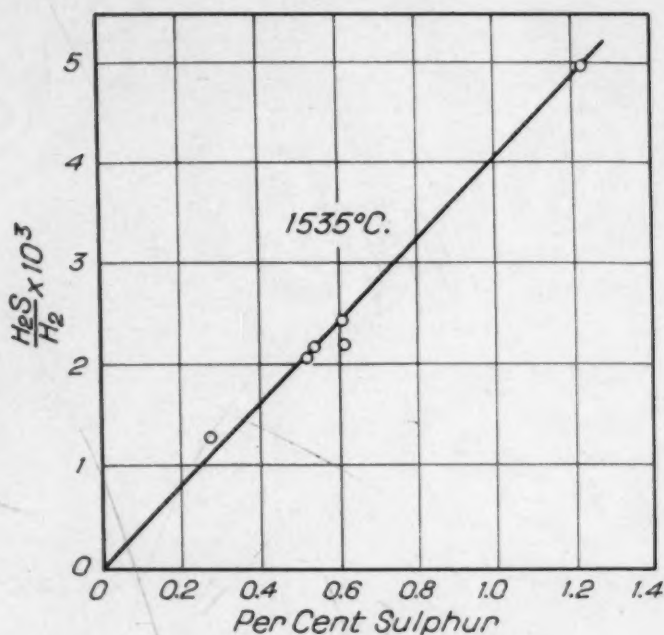


Fig. 6—Variation of Sulphur in the Iron with Ratio of H_2S to H_2 in the Gas.

from the sampling and analysis of sulphur in the melt. Most of the ingots were hollow and porous, as shown in Fig. 5. The distribution of FeS in the melt will be highly nonuniform. Unless the whole melt is analyzed, it is difficult to say that the values of sulphur analysis obtained will represent, at all times, the true composition of the melt.

DISCUSSION OF RESULTS

Form of Sulphur in Liquid Iron—The relationship between the gas and metal composition at constant temperature is shown in Fig. 6. The six points, each representing a result obtained in a silica crucible, are fitted by a straight line which shows that the percentage of sulphur is proportional to the ratio, H_2S/H_2 in the gas. This proportionality indicates clearly that the solute contains one atom of

sulphur per molecule. It is conceivable that the solute might be Fe_2S or simply atomic S, but it is far more probable that it is the compound FeS . The fact that the proportionality extends up to 1.2

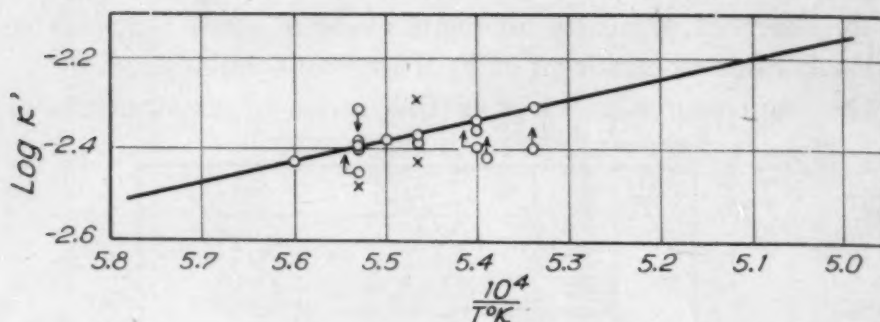


Fig. 7—Variation of Log K' with Reciprocal of Temperature. Data Obtained from Runs Using Silica Crucibles.

per cent sulphur indicates that the system conforms to the ideal solution laws up to this concentration. The results of all of these runs at 1535 degrees Cent. may be expressed by the constant,

$$K' = \frac{(\text{H}_2\text{S})}{(\text{H}_2) \times (\% \text{ S})} = 4.1 \times 10^3$$

Effect of Temperature—Results are most readily compared graphically by plotting the logarithm of K' against the reciprocal of the absolute temperature, which should, theoretically, produce a straight line. The results in silica crucibles are thus plotted in Fig. 7. Of this group, a number of runs appear definitely to have reached a state of equilibrium. This conclusion is reached from the fact that in these runs there was very little change in composition during the two hours or more of heating and the composition of the gas was unchanged by contact with the melt. These results are represented by circles. In other runs there was a distinct change in composition, indicating that the reaction was continuing and probably had not reached equilibrium during the time of the run. These points are plotted with an arrow to indicate the direction in which the reaction was progressing. The straight line drawn through the points of Fig. 7 represents our best value for the equilibrium constant in the range 1500 to 1600 degrees Cent. Its equation is:

$$\log K' = -4500/T + 0.095 \quad (2)$$

The results obtained in magnesia and porcelain crucibles are shown in Fig. 8. In these runs there was always a distinct change

in the composition of the gas as it passed through the furnace. The question arises as to whether the metal is more nearly in equilibrium with the entering or with the out-flowing gas. Both sets of points are shown in the figure, and the area between is shaded. The equilibrium line should lie within this shaded area.

It seems probable that the metal is most nearly in equilibrium

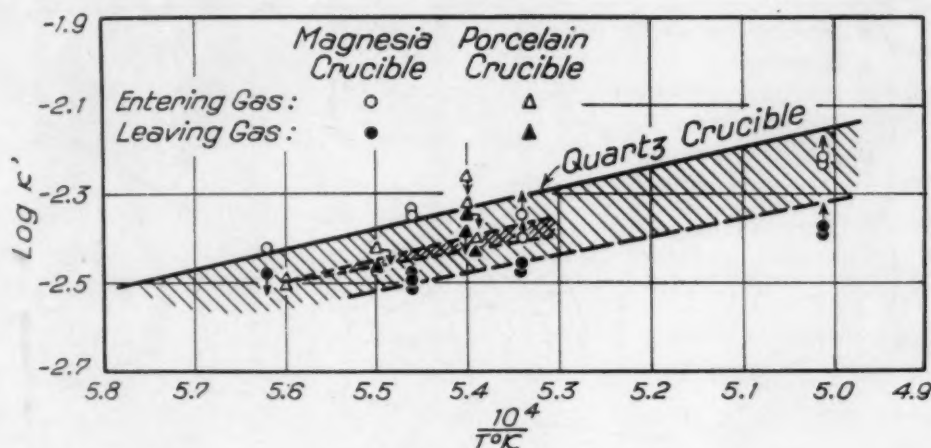


Fig. 8—Comparison of Results Obtained with Different Kinds of Crucibles.

with the entering gas, since the gas is directed toward the metal surface, and since the reaction between gas and crucible material occurs principally after the gas has passed the metal surface. The equilibrium should, therefore, be represented by the upper edge of the shaded area of Fig. 8. This edge agrees very closely with the results obtained in silica crucibles.

Comparison with Other Investigators—In order to compare the results with those of other investigators who have studied the system iron-sulphur-hydrogen, it will be convenient to express the concentrations of iron and iron sulphide in the liquid metal as mole fractions rather than as per cent. Recalculated to this basis, the results are expressed as follows:

$$K = \frac{(H_2S) \times (Fe)}{(H_2) \times (FeS)} \quad (3)$$

$$\log K = -4500/T + 1.853 \quad (4)$$

The equilibrium in the reaction of solid iron sulphide with hydrogen to produce solid iron has been studied by Jellinek and Zakowski (3), by Britzke and Kapustinsky (4), and by Bierner (5). Their results may be extrapolated to higher temperatures by the aid

of the heat capacities and heats of fusion of the substances involved in the reaction. Their data are shown in Fig. 9 by the three rather discordant lines at the left of the figure. The extrapolation of the data of Britzke and Kapustinsky (which seem to be the best of the three) to higher temperatures is indicated by the broken line. The

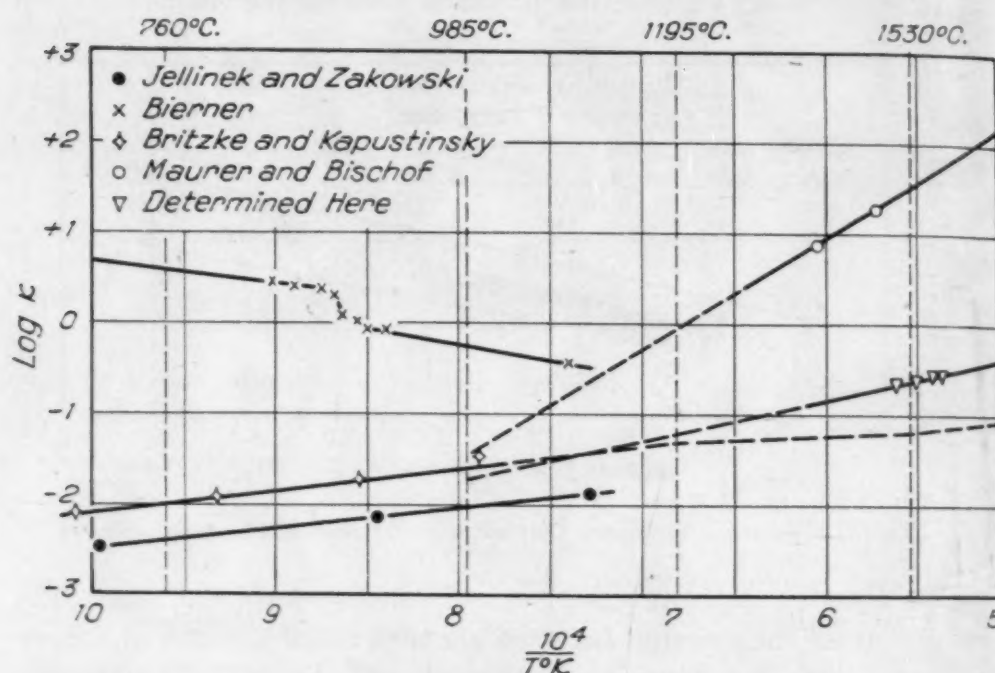


Fig. 9—Comparison of Data Obtained by Different Investigators.

extrapolation is based upon the adequate thermal data assembled by Kelley (6). Our results are shown by the triangles at the right and the heavy line drawn through them represents Equation 4. The agreement with the line extrapolated from lower temperatures is better than might have been anticipated.

The reaction in liquid iron-sulphur alloys has also been studied by Maurer and Bischoff (7), whose results are shown by the line at the upper right. Their values of K are about one hundred times as large as ours, and it would appear that the accuracy of their results has suffered from some source of error which they did not suspect. They used beryllia crucibles, and it seems probable that in their apparatus sulphur was absorbed more rapidly by the crucible than by the iron.

THERMODYNAMIC CALCULATIONS

In order to apply the results of our experiments to some of the

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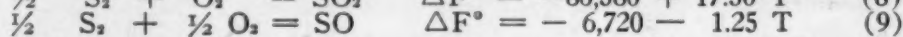
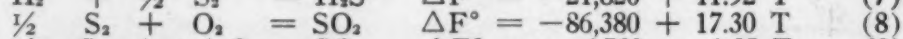
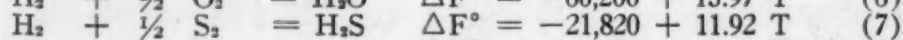
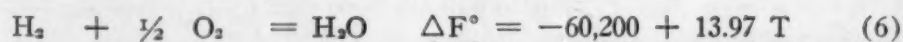
Table V
Thermodynamic Properties of Gases

	Free Energy $F^\circ - E^\circ$ $-(T)$		Entropy S°		Heat Capacity C_p	
	298.1	1873°	298.1	1873°	298.1	1873°
H ₂	24.436	37.21	31.23	44.49	6.89	8.07
O ₂	42.081	55.59	49.02	63.64	7.02	8.96
S ₂	47.242	61.70	54.42	70.19	7.75	8.98
H ₂ O	37.179	52.685	45.10	62.34	8.00	11.88
H ₂ S	41.174	57.31	49.15	67.67	8.12	12.67
SO ₂	50.95	69.42	59.40	81.44	9.51	13.58
SO	46.07	59.98

practical problems of steel making, it will be desirable to assemble the available data on a number of the compounds of sulphur and the substances with which they react. The property of especial interest is the free energy, for when this is known for each substance taking part in a reaction, the equilibrium constant of the reaction is easily obtained from the change in free energy as shown by the equation,

$$\Delta F^\circ = -4.575 T \log K \quad (5)$$

Gases—The properties of the gases in which we are interested are known with considerable accuracy, thanks to recent computations based upon precise spectroscopic data. The free energy, entropy, and heat capacity of several gases at 298.1 and 1873 degrees Kelvin (25 and 1600 degrees Cent.) are shown in Table V. These data are obtained from the publications Giauque (8), Johnston (9), Gordon (10), Kassel (11), and Cross (12), and their several co-workers. The total energy, free energy, and entropy changes which accompany the formation of the gaseous compounds from their gaseous elements are shown in Table VI. From them we find the following equations which may be employed without significant error in the range 1500-2200 degrees Kelvin (2300-3500 degrees Fahr.).

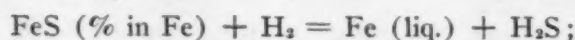


Ferrous Sulphide—The free energy of iron sulphide in liquid iron is obtained by combining the results of our experiments with Equation 7. For this purpose, the experimental results are expressed in terms of the percentage of iron sulphide in the metal and the equilibrium constants recalculated to this basis. The result is given in the

Table VI
Energy of Formation of Compounds from Their Elements

	Temp. °K.	H ₂ O	H ₂ S	SO ₂	SO
ΔE°	0.0	-57,110	-19,620	-85,860	-6,560
ΔF°	298.1	-54,637	-17,570	-81,460	-6,980
ΔF°	1873	-34,030	+ 510	-53,980	-9,060
ΔS°	298.1	- 10.64	- 9.29	- 16.83	...
ΔS°	1873	- 13.97	- 11.92	- 17.30	+ 1.25
ΔH	1873	-60,200	-21,820	-86,380	-6,720

following equation, in which the symbol (% in Fe) signifies that the activity of FeS is equal to its percentage, and that its standard state is a one per cent solution in liquid iron:

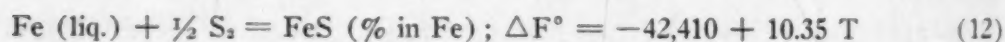


$$K = \frac{(\text{H}_2\text{S})}{(\text{H}_2) \times (\% \text{ FeS})}; \log K = -4,500/T - 0.343 \quad (10)$$

The free energy change in the reaction is, therefore, (by Equation 5):

$$\Delta F^\circ = 20,590 + 1.57 T \quad (11)$$

and when this is combined with Equation 7, we find the free energy of formation of iron sulphide dissolved in liquid iron at a concentration of one per cent,

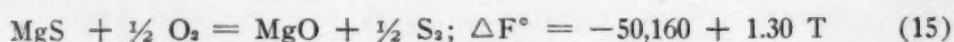
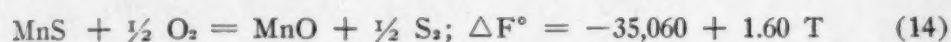


Other Sulphides and Oxides—The free energies of several sulphides and oxides will be of interest in computing the desulphurizing powers of slags. For the most part, these must be obtained from the heat of formation and entropy, and by upward extrapolation from room temperature. Although data of this sort are much less accurate than those shown above, they will serve for making some useful approximate calculations. The data in Table VII are assembled from several sources. The entropies are quoted from Kelley (13). The heats of formation of CaS and MgS are the old values of Sabatier (14), as quoted by Schenck (15), while that of MnS is a more dependable value obtained by Maier (16). The data for CaO and MgO are taken from the International Critical Tables, that of MnO is the result of a recent determination of Roth (17). The heat of formation of gaseous sulphur is that computed by Gordon (10).

Table VII
Thermodynamic Properties at 25 Degrees Cent
(ΔH in Kilo-Calories)

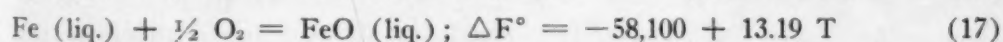
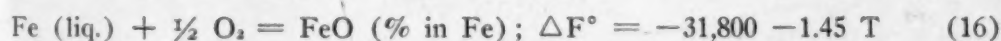
	CaO	MnO	MgO	$\frac{1}{2} O_2$	CaS	MnS	MgS	$\frac{1}{2} S_2$
ΔH	-151.8	-96.5	-145.8	0	-111.2	-45.9	-79.4	+15.54
S	9.5	14.4	6.4	24.51	13.5	18.7	...	27.21

From the data of Table VII, we obtain three useful equations which express the difference in free energy between the oxides and sulphides of the three metals.



These equations are strictly valid only at 25 degrees Cent., and the third one is uncertain with respect to the entropy of MgS. The reactions are so symmetrical that the heat effects are likely to be nearly constant, and in the absence of specific heat data, the equations may be used as approximations at the temperature of liquid steel.

The free energy of ferrous oxide in liquid iron at 1600 degrees Cent. has been accurately determined by Fontana and Chipman (2). At other temperatures it may be estimated from the approximate temperature coefficient previously reported by Chipman (18). The resultant equations for its free energy in liquid metal and slag are:



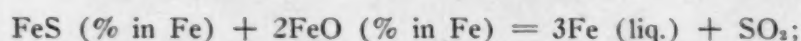
APPLICATION TO STEEL REFINING

The foregoing data are sufficient to answer many—though by no means all—of the questions which have arisen from time to time regarding the removal of sulphur from liquid steel or the prevention of its absorption.

Desulphurization with Hydrogen—The possibility of removing sulphur from liquid steel by bubbling hydrogen through the bath can be directly computed from the results of our experiments. The equilibrium constant at 1600 degrees Cent. was found to be $K' = (H_2S)/(H_2 \times \%S) = 4.9 \times 10^{-3}$. If we wish to reduce the sulphur

content of iron from 0.040 to 0.020 per cent, the average H_2S content of the exit gas will be $4.9 \times 10^{-3} \times 0.030 = 0.147 \times 10^{-3}$ or about fifteen parts per hundred thousand. The removal of 0.02 per cent sulphur from one ton of steel would produce about five cubic feet of H_2S , which would require approximately 33,000 cubic feet of hydrogen. Clearly, such a process would be out of the question.

Desulphurization by Vacuum Treatment—Perhaps it might be possible to remove sulphur from an oxidized bath by melting in vacuum, and pumping off sulphur dioxide. The reaction and its free energy are obtained from Equations 8, 12, and 16:



$$\Delta F^\circ = + 19,630 + 9.85 T \quad (18)$$

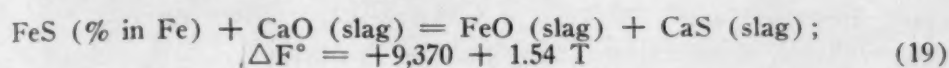
$$K = \frac{(\text{SO}_2)}{(\% \text{ FeS}) (\% \text{ FeO})^2}; \log K = -4,290/T - 2.15$$

At 1600 degrees Cent., $K = 3.6 \times 10^{-5}$, and when this is solved for a sulphur content of 0.020 and an iron oxide content of 0.36 per cent, it is found that the pressure of sulphur dioxide is 2.57×10^{-6} atmospheres or about 0.002 millimeter. A vacuum such as this is can be obtained in the laboratory, but is scarcely to be considered for melts larger than a few ounces. A similar calculation shows that the pressure of sulphur monoxide would be of the order of 10^{-8} millimeters. In fact, the data of Table VI show that in all cases at steel-making temperatures the formation of SO is altogether negligible in comparison with SO_2 .

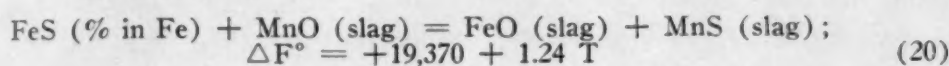
Slag-Metal Reactions—The reactions to which we owe the desulphurizing powers of basic slags are those in which a basic oxide in the slag reacts with iron sulphide in the metal to form iron oxide and a more stable sulphide. In order to write the free energy equation for such a reaction, it is necessary to combine the appropriate equation—13, 14, or 15—with Equations 12 and 17. This combination leads to the three equations and their corresponding equilibrium constants as shown below. Strictly speaking, these equations should be applied only to the solid sulphide and solid oxide of the basic element; but the energy changes involved in the fusion of the solids are small and tend to balance one another. The minor uncertainty occasioned by their omission can be corrected only when more complete data are available. For the present purposes, we shall apply the

equations to the oxides and sulphides as they exist in slags, expressing their activities as mole fractions of the free oxide or sulphide.

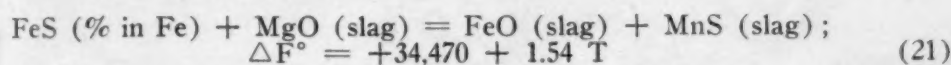
The desulphurization equations are:



$$K = \frac{(\text{FeO}) (\text{CaS})}{(\% \text{ FeS}) (\text{CaO})}; \log K = -2047/T - 0.337$$



$$K = \frac{(\text{FeO}) (\text{MnS})}{(\% \text{ FeS}) (\text{MnO})}; \log K = -4234/T - 0.271$$



$$K = \frac{(\text{FeO}) (\text{MgS})}{(\% \text{ FeS}) (\text{MgO})}; \log K = -7530/T - 0.337$$

Table VIII
Equilibrium Constants in Desulphurization by Basic Oxides

Temperature Degrees Cent.	1500	1600	1700
CaO-CaS	0.032	0.037	0.042
MnO-MnS	0.0022	0.0029	0.0038
MgO-MgS	2.6×10^{-5}	4.6×10^{-5}	7.0×10^{-5}

The equilibrium constants of the three slag-metal reactions are shown at three temperatures in Table VIII. A number of conclusions may be reached from these data. The first is that lime is a more potent desulphurizer than either of the other oxides, with MnO second and MgO a poor third. This should not be interpreted as conflicting with the data of Holbrook and Joseph (19) on blast furnace slags since the present calculations have to do with limiting conditions only, whereas their measurements involved only the speed of the reaction. A second conclusion is that an increase in temperature produces a slight increase in desulphurizing power. In general, it produces an even more marked increase in the speed of the reaction, thus exerting a double effect upon the final sulphur content of the metal.

In order to apply the calculations quantitatively to open-hearth results, it is necessary to convert percentages of lime, FeO, etc., to mole fractions in the slag. There is no recognized method of making this conversion, since the nature and degree of dissociation of the

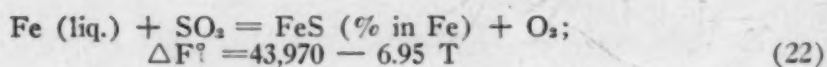
compounds in the slag are not known with certainty. As a first approximation, we may assume that in basic slag the silica is held as dibasic silicates of the type $2 \text{CaO} \cdot \text{SiO}_2$, and the phosphorus as tri-basic phosphates of the type $3 \text{CaO} \cdot \text{P}_2\text{O}_5$. The free CaO is then obtained by subtracting from the total number of moles of base, $\text{CaO} + \text{MnO} + \text{MgO}$, twice the number of moles of SiO_2 , and three times the number of moles of P_2O_5 . The data of Table IX are taken from the published work of Diehl (20). The mole fraction of CaO is computed as outlined above, while that of FeO disregards any tendency of this oxide to combine with other constituents of the slag. The total sulphur content of the slag is computed as CaS , and that of the metal as FeS . The ratio corresponding to the equilibrium constant in the lime-iron sulphide reaction is shown in the last line of the table. These figures are in agreement, at least as to order of magnitude, with the calculated equilibrium constant 0.037 at 1600 degrees Fahr. This may be taken to indicate that the desulphurization equilibrium is at least approached in open-hearth operation, and that the most important variable affecting it is the free lime.

Table IX
Desulphurizing Power of Open-Hearth Slags;
Data from Diehl (20)

Heat No.	82096	93172	85241	73259	83254	83261	81292
CaO , Mol Fr.	0.317	0.197	0.129	0.420	0.507	0.537	0.547
FeO , Mol Fr.	0.192	0.183	0.236	0.252	0.207	0.230	0.250
CaS , Mol Fr.	0.0027	0.0033	0.0032	0.0081	0.0064	0.0084	0.0112
FeS Metal % (FeO) (CaS)	0.102	0.099	0.069	0.126	0.091	0.093	0.113
(% FeS) (CaO)	0.016	0.031	0.085	0.038	0.029	0.039	0.045

Reactions Between Gas and Bath—A number of reactions may occur by which sulphur is transferred from combustion gases to the slag and to the metal. In the flame practically all of the sulphur in the fuel is converted into sulphur dioxide, and it will be unnecessary to consider either H_2S , S_2 , or SO . This statement may easily be verified by simple computations based upon Equations 7, 8, and 9.

The reaction by which Herty (21) and Maurer and Bischoff (7) account for absorption of sulphur from the gases is written below, along with its free energy expression obtained by combining Equations 8 and 12:

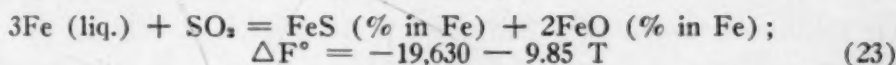


When this is solved for a temperature of 1800 degrees Kelvin (2780 degrees Fahr.), the melting point of iron, we find

$$K = \frac{(O_2) (\% \text{ FeS})}{(SO_2)} = 1.5 \times 10^{-4}$$

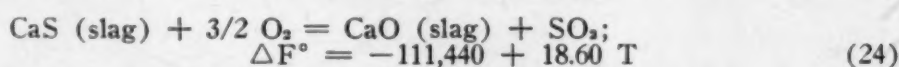
If this is the controlling reaction, then in a gas mixture containing as much oxygen as sulphur dioxide no sulphur pick-up should occur above 0.00015 per cent FeS, and any sulphur in excess of this amount should be oxidized to SO_2 . Why, then, does sulphur absorption occur? If the above reaction is effective, why can't we desulphurize the bath by providing a little excess air in the flame? The answer is that the reaction is not effective because the oxygen which comes in contact with the iron is all used up in forming iron oxides. An oxidizing flame is conducive to desulphurization or to a decreased sulphur pick-up, but the mechanism is more indirect than Equation 22 would indicate.

The reaction of iron with sulphur dioxide is more correctly represented by the equation,



The equilibrium constant at the melting point is 2.3×10^4 , which signifies that sulphur dioxide in contact with the iron would be almost entirely absorbed. A function of excess air is, therefore, to prevent this contact during melting by producing a protective oxide film.

When the bath is covered by slag so that the gases do not come into intimate contact with the metal, some removal of sulphur from the slag by oxidation may occur. The reaction is,

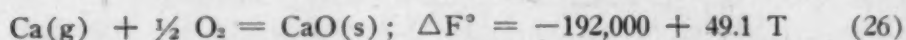
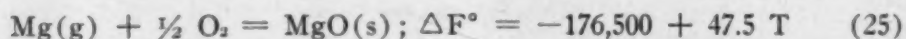


The equilibrium constant at 1600 degrees Cent. is about 2×10^9 and the reaction, therefore, has a strong tendency to occur. Other substances in the slag are competing with CaS for the small amount of oxygen that is available. Suspended droplets of iron are being oxidized, FeO absorbs oxygen to form Fe_2O_3 , and finally the CO evolved from the bath is burning to CO_2 . It is the interference of these reactions which prevents efficient desulphurization of the slag by excess air in the flame.

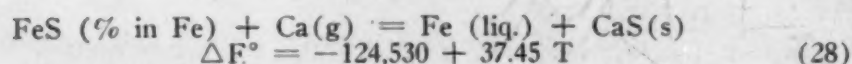
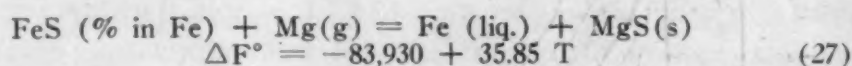
Metallic Desulphurizers—The affinity of some metals for sul-

phur is so great that under proper conditions it should be possible to effect a marked reduction in sulphur content by addition of the metal itself. It is well known that manganese will decrease the sulphur content of high-sulphur pig iron by forming manganese sulphide, which is thrown out of solution with the kish. In the open-hearth, however, the desulphurizing power of manganese is offset by the reaction of its sulphide with FeO to form manganese oxide. If we compute, thermodynamically, its desulphurizing power, we find the same result as if we had based the calculation on a concentration of MnO in the slag which is in equilibrium with manganese in the metal. In the open-hearth, we cannot, in the present state of our knowledge, differentiate between the desulphurizing power of manganese and that of its oxide. Since the usual slag contains much more CaO than MnO, and since the desulphurizing power of the former is distinctly greater, we must conclude that the influence of manganese as a desulphurizer in the open-hearth is far less important than that of lime. This conclusion is in agreement with the experimental results and critical discussion of Bardenheuer and Geller (22).

Calcium and magnesium form stable sulphides, and, in a bath which has been thoroughly deoxidized, their desulphurizing powers might be used to advantage. It is possible to compute the concentration of FeS which would be left in the bath, if enough calcium or magnesium is added to react with substantially all of the oxygen and to leave the bath saturated with the free metal after equilibrium with sulphur has been established. Calcium and magnesium are gases at the temperature of liquid steel, and their solubility in the bath is quite limited. The free energy of formation of the oxides from the respective gaseous metals and oxygen was used in computing their deoxidation equilibria (18). The equations are,



When these equations are combined, respectively, with 15 and 13, and the result added to Equation 12, the following expressions are obtained:



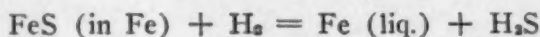
The equilibrium constants obtained from these equations for a temperature of 1600 degrees Cent. are:

$$\begin{aligned} (\% \text{ FeS}) \quad (\text{Mg}) &= 1.1 \times 10^{-2} \\ (\% \text{ FeS}) \quad (\text{Ca}) &= 4.3 \times 10^{-6} \end{aligned}$$

If the bath is saturated with the metal so that the partial pressure of the gaseous metal is one atmosphere, then (Mg) and (Ca) are equal to unity, and the percentage of FeS in the bath is equal to the value of the product. Thus, the sulphur present as FeS is reduced to 0.0045 per cent by the magnesium reaction or to an astonishingly low value of 1.8×10^{-6} per cent by desulphurization with calcium.

SUMMARY

A thorough study has been made of the condition of equilibrium in the reaction,



The precautions necessary for obtaining dependable equilibrium data in this reaction are described in detail, and the results of numerous experiments are presented, in which equilibrium is approached from the high-sulphur and low-sulphur sides.

The experimental data are summarized by the equation,

$$K' = (\text{H}_2\text{S})/(\text{H}_2) (\% \text{ S}); \log K' = -4,500/T + 0.095$$

The results are somewhat higher than would be expected from extrapolations of low-temperature data, but are about a hundredfold lower than the data of Maurer and Bischoff on the same reaction.

The free energies of FeS and a number of other sulphides and oxides are computed from the experimental results and from data in the literature.

The thermodynamic treatment of several possible reactions involving sulphur in liquid iron shows that:

1. Removal of sulphur from liquid steel by hydrogen requires so much hydrogen as to make the process impracticable.
2. Removal of sulphur by vacuum treatment would require a high vacuum obtainable only in very small furnaces.
3. In the desulphurization of liquid steel by slag in the open-hearth process, the most important variable is the free

lime in the slag. MnO and MgO are less potent desulphurizers. An increase in temperature promotes desulphurization.

4. In the open-hearth flame, sulphur exists as sulphur dioxide. This gas is completely absorbed when it comes in contact with liquid iron. Excess oxygen in the gas helps to prevent its absorption by formation of an oxide film. Oxygen tends to desulphurize the slag by oxidizing calcium sulphide to sulphur dioxide.

5. The desulphurizing power of metallic manganese is essentially equivalent to that of an equilibrium amount of manganese oxide in the slag. Magnesium and calcium exert a powerful desulphurizing action, provided oxygen is absent.

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DISCUSSION

Written Discussion: By J. C. Warner, associate professor of metallurgy, Carnegie Institute of Technology, Pittsburgh.

This paper reports a valuable addition to the list of investigations by Dr. Chipman and his collaborators. When one considers the distinct progress which has been made in obtaining improvements and a better understanding of the steel-making process through a small number of investigations into the physical chemistry of pertinent reactions, one wonders why more research of this type is not undertaken. One obvious reason for the lack of more activity in this field is the inherent difficulty of making reliable measurements at steel-making temperatures. However, investigations such as the present one show that such measurements can be made with fair precision and in addition to supplying useful information they contribute to the technique of high temperature measurements.

Once an equilibrium constant has been obtained, directly or indirectly, the principal difficulty encountered in applying thermodynamics to steel-making reactions, as has been done by Chipman, Herty and others, is the lack of information concerning the chemical potentials or activities of the substances involved in the equilibrium in the slag and metal phases. Note, for example, the approximations which Dr. Chipman found it necessary to make concerning the activities of CaO, MnO and MgO in his estimate of the desulphurizing action of these substances in slags. A detailed investigation of the activities of the components of the slag and metal phases as a function of the composition and the temperature should yield results of considerable practical value.

A NEW TOOL FOR THE CONTROL OF QUALITY STEEL MAKING

By G. T. MOTOK

Abstract

A newly improved equipment for fractional vacuum extraction of gases and oxides for the first time has been used for steel-making control. The routine chemical analysis does not supply enough information regarding the composition of the steel when there is a difference in physical and mechanical properties of the material. The improved fractional extraction equipment affords an accurate determination of gases and a differentiation of the different types of oxides which, though in small amounts, may affect considerably the service performance of the steel.

Results obtained with this equipment indicate that rimming steel, as expected, has high oxygen content as FeO and some as Al_2O_3 .

During welding, metals take up nitrogen, and some of the elements in steel, mainly manganese, become oxidized.

Killed high carbon steel shows a greater oxygen content as SiO_2 and Al_2O_3 than rimming steel. A small increase in either of these two oxides may produce material of inferior quality.

The results for a double check fractional extraction of gases and oxides in steel may be obtained in less than eight hours. With this equipment as many as ten different samples may be tested for total oxides and gases in eight hours.

EXTENSIVE research work has shown that scientific control of steel-making contributes to the improvement in the quality of the steel produced. This is made evident by the fact that certain steels possess specific, inherent properties which are intimately connected with the method of manufacture, especially with the deoxidation practice. These inherent properties of steel are difficult to explain by the ordinary chemical and physical tests and affect greatly the commercial processing of the finished steel.

It is a problem of the steel maker, therefore, to determine the

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underlying metallurgical causes for these different inherent characteristics. This can be attempted by studying the high temperature reactions, the separation of the reaction products and the relation of the amount of these products left in the finished steel, as factors affecting the quality of the steel. Once this knowledge is acquired, it must be applied systematically to every phase of the steel-making process, with the object of producing steel that will be uniform throughout the heat as well as from heat to heat.

GASES AND THE GRAIN SIZE

Gases, as well as the control of the grain size, are important factors in explaining many of the hitherto unexplained differences in inherent characteristics of steel. The subject of gases and their effect in metals has at different times received considerable attention, but it is evident that more work could be done on this subject. Of interest to the practical metallurgist, in a study of gases in metals, is the finding out of the possible effect of gases on the properties of steel and the importance of these effects in relation to the small quantity of gas which may be found in commercial steels.

A well known influence of temperature on the quantity of gas absorbed by a metal is due to the allotropic changes in the structure of the metal. It is reasonable to assume that gas dissolved in metal might not be objectionable provided it remains in solution in both liquid and solid states, and provided also that there is no difference in solubility in these two states.

Nitrogen—That the amount of gas absorbed by a metal changes abruptly when the allotropic form changes, is illustrated by the iron-nitrogen system. At 1700 degrees Fahr. (925 degrees Cent.), at which temperature iron exists in one allotropic form, it takes 20 times as much nitrogen as it takes at 1600 degrees Fahr. (870 degrees Cent.)¹

Any gas whose solubility is greater in the liquid than in the solid metal may cause the formation of voids in the metal. Liquid solubility of nitrogen in iron² is 0.039 per cent at just above the melting point and 0.042 per cent at 3200 degrees Fahr. (1760 degrees Cent.),

¹A. Sieverts and E. Jurish, "Dissertation" Leipzig, 1912—Abstract in *Stahl und Eisen*, Vol. 34, 1914, p. 252.

²J. Chipman and D. W. Murphy, "Solubility of Nitrogen in Liquid Iron," American Institute of Mining and Metallurgical Engineers, 1935, Technical Publication, No. 591, January 1935, *Metals Technology*, p. 12.

whereas the finished solid open-hearth steel contains 0.005 per cent³ and the Bessemer steel 0.012 to 0.018 per cent nitrogen.⁴

However, nitrogen could be considered as an alloying constituent with certain definite advantages; for example, in the grain refinement of chromium steels. The aging properties of steel containing nitrogen are also of great interest. Nitrogen and phosphorus form, with the metals, compounds whose characteristics, similar to those of the carbides, more nearly approach the characteristics of metallic substance and may therefore be regarded as true structural elements of the steel.

Hydrogen—The study of hydrogen in steel must become recognized as a matter of serious practical importance. Many investigators⁵ have observed that small quantities of hydrogen in steel appreciably affect mechanical properties of the metal. The solid solubility of hydrogen is considerably less than the liquid solubility. Due to less solid solubility, hydrogen produces unsoundness similar in type to the skin holes in rimming steel.

Based on the temperature of formation of flakes as ascertained by Houdremont and Korshan⁶ and on the increase in pressure of hydrogen (decrease in solubility) with decreasing temperature, Bennek and co-workers⁷ (in Germany) have advanced the hypothesis that the tensions which call forth the formation of flakes, are precisely due to the evolution pressure of this gas.

This suggests the possibility of formation of hydrides at high temperature but which dissociate with decreasing temperatures. This postulate has been confirmed by work of Sieverts on "hydrides" of the metals.⁸

Oxygen—Large internal holes in steel are due to the hydrogen plus oxygen reaction. Oxygen is far from being a harmful constituent in steel; in some cases it may actually be beneficial.

Oxygen causes an apparent increase in the amount of pearlite, which suggests the possibility of the formation of a ternary eutectoid

³F. Wust and J. Duhr, "Über ein Stickstoff-bestimmungsverfahren in Stahl und Roheisen und über den Stickstoff bei den Hüttenprozessen," *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung*, 1921, Vol. 2, p. 39.

⁴H. Tholander, "Influence of Nitrogen on Bessemer and Open Hearth Ingot Iron," *Jernkontorets Annaler*, 1888, Vol. 43, p. 429.

⁵F. Körber and J. Mehovar, "Contribution to the Knowledge of the Changes with Time of the Mechanical Properties of Newly Rolled Rails, Particularly of Basic Bessemer Steel," *Mitteilungen Kaiser Wilhelm Institut für Eisenforschung*, Vol. 17, 1935, p. 89. *Stahl und Eisen*, Vol. 55, 1935, p. 914.

⁶E. Houdremont and H. Korshan, "The Conditions for the Occurrence of Flakes in Steel," *Stahl und Eisen*, Vol. 55, 1935, p. 297.

⁷H. Bennek, H. Schenck and H. Muller, "The Cause of the Occurrence of Flakes in Steel," *Stahl und Eisen*, Vol. 55, 1935, p. 321.

⁸A. Sieverts, "Die Aufnahme von Gasen durch Metalle," *Zeitschrift für Metallkunde*, 1929, Vol. 21, p. 37-46.

of iron, iron carbide, and iron oxide. The influence of oxygen on the carburization of steel⁹ is not clearly understood, but its importance has been emphasized by many writers.

Oxides of Carbon—Determination of oxygen content shows that the oxygen content of liquid steel in the furnace is proportional to the carbon it contains—the greater the carbon, the less the oxygen, before final deoxidizers have been added.

Carbon oxide (CO) is produced as the result of the reaction between carbon with FeO and MnO and it probably has a substantial solubility in liquid steel, but the solid solubility is slightly less than the liquid solubility.

Due to this slight difference in solubility, carbon monoxide produces very little unsoundness in steel.

Oxide of Iron—There is a critical iron oxide content in steel which is desirable and which suggests the thought that it is not necessary to completely deoxidize the steel.

Iron oxide alone is rarely observed but it is generally associated with the double oxides of iron and manganese or with sulphides. Iron oxides segregate to a considerable extent from the liquid mass at the moment of solidification.

Other Metal Oxides—Liquid steel after addition of deoxidizers contains less soluble iron oxide but an increase of insoluble manganese and silicon oxides.

Inclusions—As is known, oxygen and sulphur are the chief elements producing nonmetallic inclusions in steel. Deoxidation products consist of less refractory oxides of iron and manganese and of more refractory oxides of silicon, chromium and aluminum.

Insoluble refractory material is also picked up from nozzle, runner and ladle lining.

DETERMINATION AND IDENTIFICATION OF GASES AND OXIDES OCCURRING IN STEEL

Chemical history of a heat gives the changes in the chemical composition of the metal occurring during the making. The need of methods for determining gases in steels has long been recognized, but few such methods have come into any wide use or have given data which are sufficiently complete or concordant to permit a satis-

⁹Grain Size Symposium—Held during the 16th Annual Convention of the American Society for Metals, New York City, October 1934. Published in *TRANSACTIONS, American Society for Metals*, December 1934.

factory correlation between the gas content of steels and their qualities.

Two most frequently used methods for determination of gases in steels have been modifications of the Ledebur¹⁰ method for oxygen and of the Allen¹¹ method for nitrogen. In the Ledebur, or hydrogen reduction method, the iron oxides are reduced to metal and water, and the water is determined. This method is limited to the determination of the oxygen present as iron oxide or the high oxides of manganese (above MnO) and it fails to determine these oxides if they are combined as silicates. The Allen method for nitrogen (distillation in acid) determines principally the nitrogen which is present as nitrides of iron and manganese. Uncombined nitrogen and nitrogen present as nitrides of silicon, chromium, aluminum or some other possible alloying elements are either not at all or incompletely determined.

Therefore, it seemed desirable to develop a method for the extraction of gases from steels at high temperatures. The usual vacuum method for determination of total gases in steels does not differentiate between the combined forms in which oxygen is distributed in steel. The recent developments in the vacuum method,¹² however, afford more complete determination of gases present in steel.

The important factor in determining the quality of a steel is not in the amount of total oxygen present, but in the type and form of the combined oxides and in the amount of each combined form. Oxygen as iron and manganese oxides or other oxides with melting temperatures below that of the rolling of steel may have less harmful effect than the more refractory oxides found in steel.

To differentiate between these two general types of oxides, and also to determine them quantitatively, the vacuum fusion method by partial extraction at different elevated temperatures at which the iron, manganese, silicon, aluminum and other oxides are individually reduced, has been developed and recently improved for its use in steel-making problems.

EQUIPMENT FOR THE VACUUM EXTRACTION OF GASES

Vacuum—This improved method consists in melting a sample of

¹⁰A. Ledebur, "Aus dem Eisenhütten-Laboratorium I Sauerstoffbestimmung im Schmiedeborn Eisen," *Stahl und Eisen*, Vol. 2, 1882, p. 193-198.

¹¹A. H. Allen, "Primary Experiments to Determine the Existence of Nitrogen in Steel," *Journal, Iron and Steel Institute*, 1879, No. II, p. 480.

¹²Lewis J. Reeve, "Improvements in the Vacuum Fusion Method for Determination of Gases in Metals," *A.I.M.E.*, Vol. 113, Iron and Steel Div., 1934, p. 82-110.

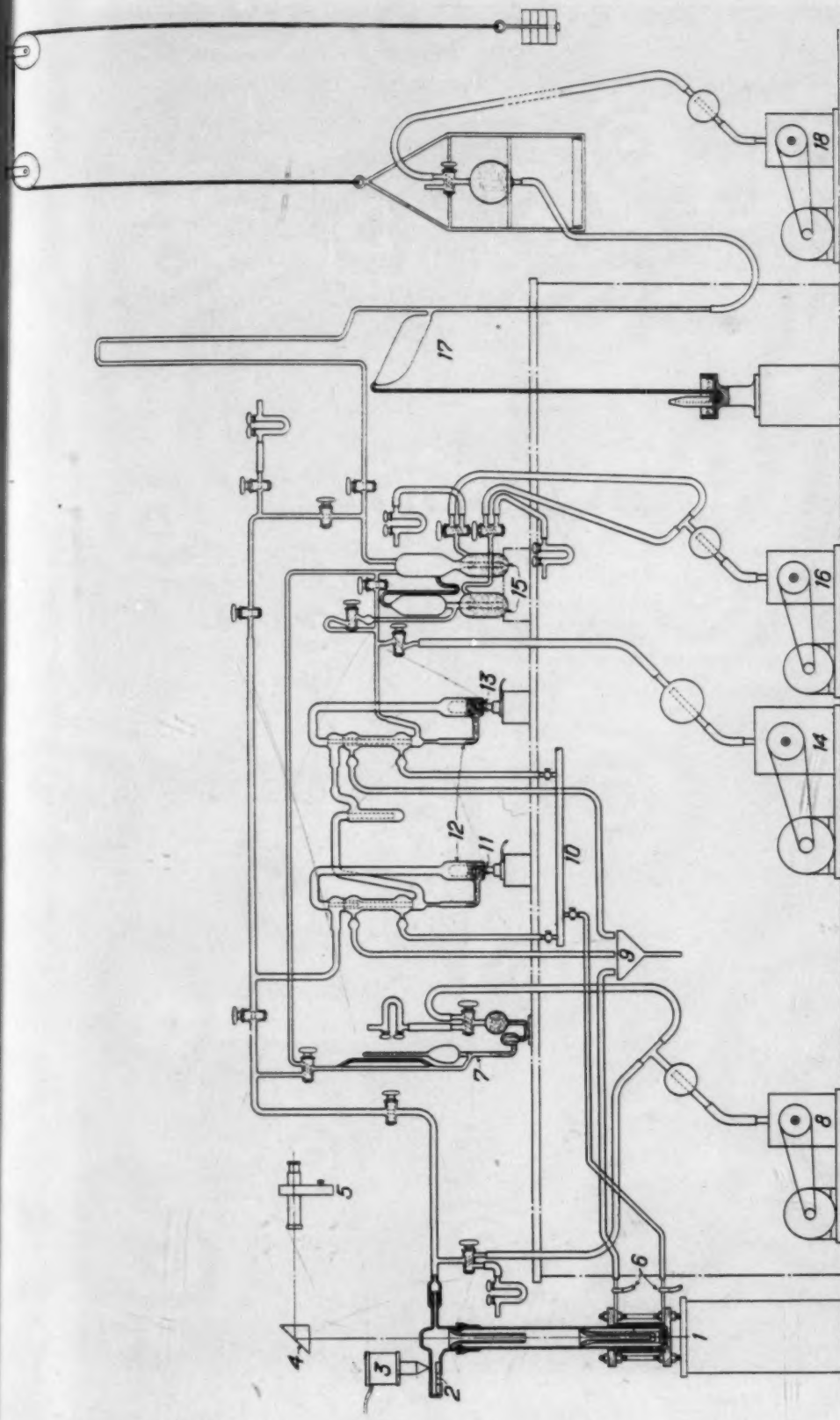


Fig. 1—Arrangement of Apparatus for Vacuum Fusion Extraction of Gases in Metals.

- | | | |
|-------------------|------------------------------|---------------------------------|
| 1—Vacuum Furnace. | 14—Vacuum Pump No. 2. | 17—Toepler Gas Collecting Pump. |
| 2—Test Pieces. | 15—Gas Collecting Reservoir. | 18—Vacuum Pump No. 4. |
| 3—Magnet. | 16—Vacuum Pump No. 3. | |
| 4—Prism Mirror. | 10—Cooling Water Supply. | |
| 5—Pyrometer. | 11—Heater. | |
| | 12—Mercury Diffusion Pumps. | |
| | 13—Heater. | |

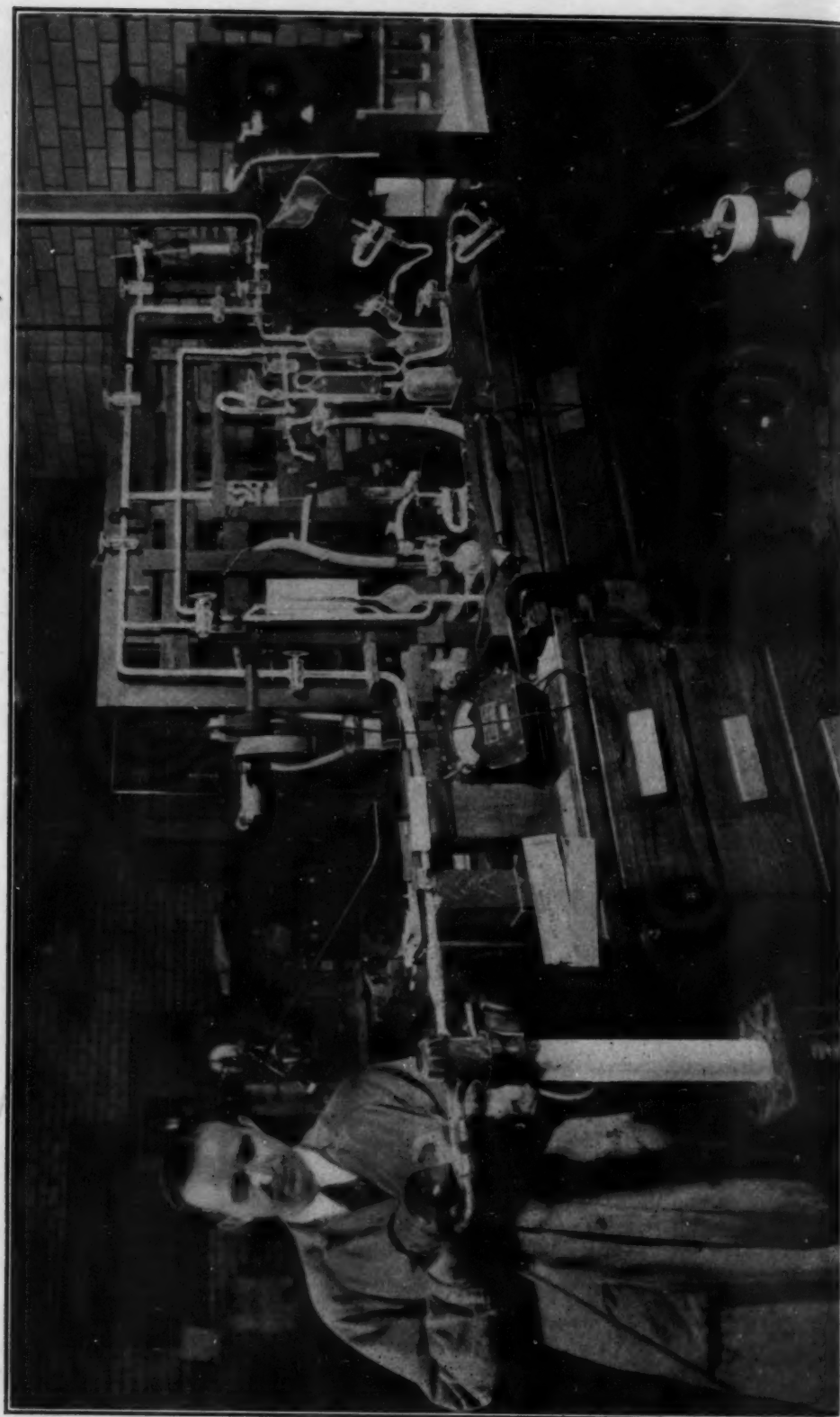


Fig. 2—Photograph Showing the Front View of Apparatus.

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steel, to which a low melting point metal such as tin is added, in a graphite crucible in a very high vacuum. With this equipment a vacuum of the order of 0.0000001 millimeter or better is reached before the heating of the sample is started.

The vapor pressure of the alloy increases with temperature as it is expected. Such high vacuum is maintained by means of four megavac vacuum oil pumps and two mercury diffusion pumps.

Furnace—An Ajax high frequency equipment supplies the power to the furnace coil. The silica tube is the largest size used for such vacuum work. The graphite crucible inside the silica tube is large enough to hold samples up to 250 grams in weight.

Glass Tubing—Glass tubing is one continuous glass member from the point where it is sealed to the furnace, to the other end where the gases evolved are collected over mercury in a vial, Fig. 1.

In Fig. 2 is shown the front view of the apparatus, while in Fig. 3 the back view shows the vacuum pumps, and in Fig. 4 the gas analysis apparatus is shown.

EXTRACTION OF GASES

Before the power is turned on, a vacuum is obtained throughout the entire apparatus. Then the empty graphite crucible is heated for some time at 3400 degrees Fahr. (1870 degrees Cent.) in order to eliminate all the gases existing in the crucible.

After this is accomplished, the temperature is lowered and the low melting point metal is dropped in the crucible in order to extract any gases that might occur in such metal. Thus there is no need for considering any correction blank in extracting gases.

Next the steel sample is dropped in the crucible and the temperature is raised to the first extraction temperature. Temperatures are measured with the optical pyrometer, Fig. 3.

Temperature of Extraction—In making the fractional determination, different temperatures of extractions are necessary for different grades of steel. In plain carbon steels which may have inclusions containing oxides of iron, manganese, silicon and aluminum, four temperatures of extractions are needed. In other steels containing different alloying elements different temperatures of extraction are used. The temperature of extraction depends on the reactivity of the carbon, taken by the metal from the graphite crucible, and the re-



Fig. 3—Photograph Showing Back View of Apparatus.

Fig. 3—Photograph Showing Back View of Apparatus.

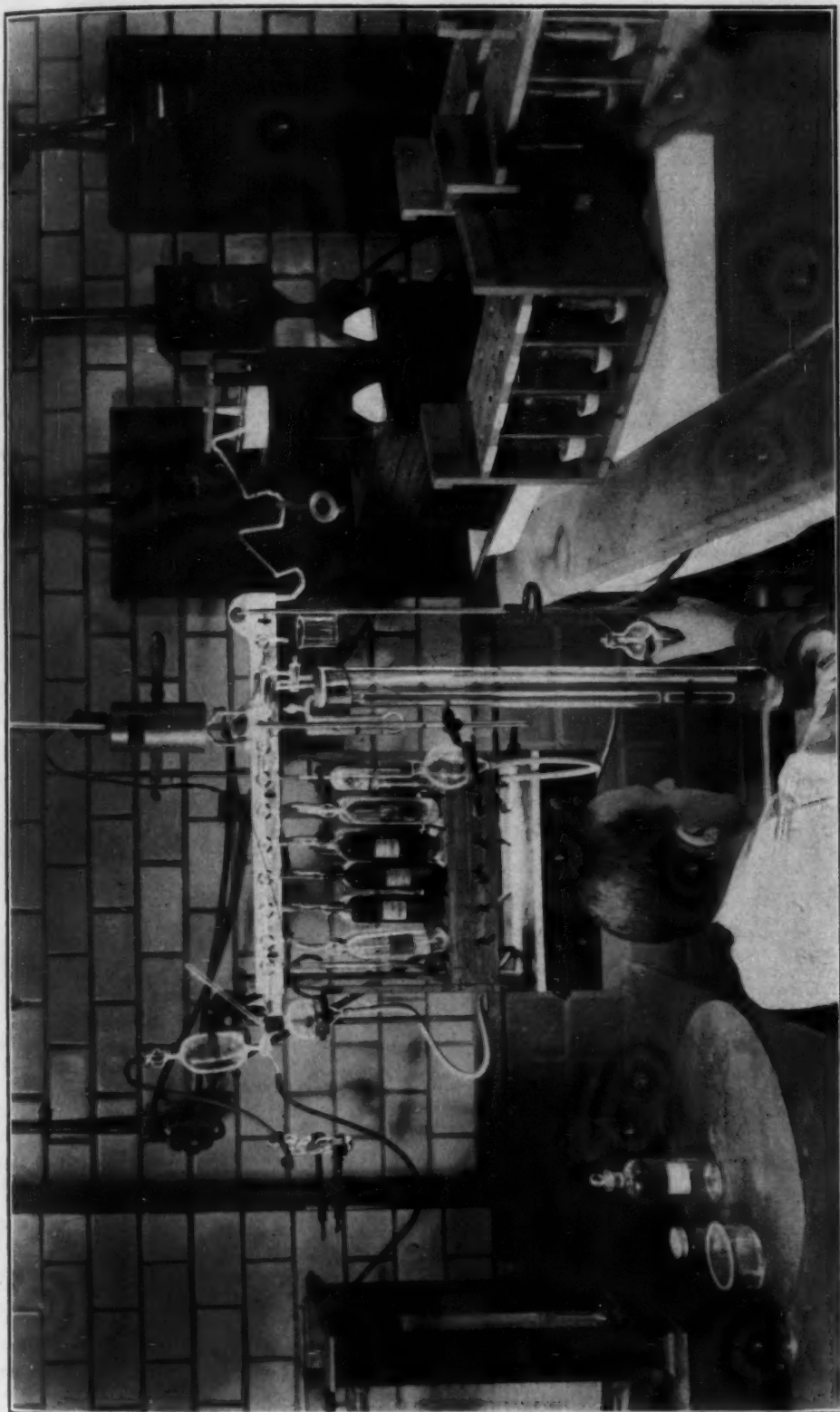


Fig. 4—Photograph Showing the Gas Analysis Apparatus.

Table I
Fractional Extraction of Oxides and Gases in Different Typical Ferrous Materials

1. Semi-Rimming Plate Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Percentage of		
		Oxygen	Hydrogen	Nitrogen
1960	FeO	0.00024	0.0011
2140	MnO	0.0095	0.0022
2410	SiO ₂	0.01075	0.00008	0.0011
2860	Al ₂ O ₃	0.0057	0.00016	0.0011
Total		0.02595	0.00048	0.0055
2. Shielded Arc Deposit				
1960	FeO	0.0011	0.00014
2140	MnO	0.0172	0.00014
2410	SiO ₂	0.0521	0.00056	0.0049
2860	Al ₂ O ₃	0.0071	0.0010
Total		0.0775	0.00084	0.0059
3. Bare Weld Metal				
1960	FeO	0.0323	0.00057	0.0970
2140	MnO	0.2395	0.00014	0.0534
2410	SiO ₂	0.0085	0.00036	0.0386
2860	Al ₂ O ₃	0.0266	0.0010
Total		0.3069	0.00107	0.1900
4. Open-Hearth Iron				
1960	FeO	0.04668	0.00019	0.0092
2140	MnO	0.00904	0.00056	0.0013
2410	SiO ₂	0.00527	0.00037	0.0026
2860	Al ₂ O ₃	0.01205	0.00066
Total		0.07304	0.00178	0.0131

spective oxide inclusions. Bauholz,¹³ Meyer,¹⁴ Rieber¹⁵ and others have determined the temperatures of dissociation of nitrides and of reaction of oxides with the carbon in vacuum.

Collecting and Analysis of the Gases—Gaseous products evolved are collected over mercury and analyzed in a special gas analysis apparatus, Fig. 4. An amount as small as 0.2 cubic centimeters can be analyzed by diluting this small amount with a purified gas. By this method of extraction of gases and oxides and by analyzing the gases as such, any possibility of blank corrections needed when gas absorbents are used is eliminated.

Applications—The usefulness of this equipment as a means of steel-making control is evident from the results in Table I and their interpretation.

In semi-rimming plate steel there is more oxygen as SiO₂ than the other oxides, indicating that the steel was semi-killed with ferro-silicon.

¹³W. Bauholz and R. Durrer, "The Primary Reaction of Metallic Oxides with Solid Carbon," Iron and Steel Institute, Carnegie Scholarship Memoirs, Vol. 23, 1934, p. 1-12.

¹⁴Oskar Meyer, "Über den Verlauf der Reaktionen zwischen Graphit und Oxyden sowie zwischen Schwer-Metallkarbiden und Oxyden," *Archiv für das Eisenhüttenwesen*, Vol. 4, 1930, p. 193-198.

¹⁵Jean Rieber, "Beiträge zur Kenntniss der Metallnitride Doctor's Thesis," Technische Hochschule, Hanover, 1930, 45 pages.

In open-hearth iron the maximum oxygen content is in form of FeO, as is usually found in rimming steels.

IMPACT STRENGTH VERSUS GASES AND OXIDES

During testing for impact strength two high carbon steels which were practically identical as far as manufacture, heat treatment, McQuaid-Ehn, and other properties are concerned, it was found that heat 60 was far inferior to heat 73. Fractional extraction of gases and oxides shows more oxygen as Al_2O_3 in heat 60 than in heat 73.

Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Heat 73			Heat 60		
		% O ₂	% H	% N	% O ₂	% H	% N
1960	Free O ₂ and FeO	0.00363	0.00094	0.00129	0.000054
2140	MnO	0.0076	0.000082	0.00215	0.000054	0.00075
2410	SiO ₂	0.0142	0.000205	0.00805	0.00430	0.000268	0.00075
2760	Aluminum Silicate	0.0399	0.000327	0.01435	0.01634	0.00107
3000	Al ₂ O ₃	0.02605	0.000531	0.00287	0.09933	0.000589	0.00449
Total		0.09138	0.002085	0.02525	0.12341	0.002035	0.00599

Welding Rods				
Temp. of Extraction Deg. Fahr.	Good Probable Oxides Reduced	Percentage of		
		Oxygen	Hydrogen	Nitrogen
1960	FeO
2140	MnO	0.0126	0.00064	0.0020
2410	SiO ₂	0.00285		0.0010
2860	Al ₂ O ₃	0.00228	0.00057
Total		0.01539	0.00121	0.0030
1960	Bad FeO	0.00352	0.00021	0.0051
2140	MnO	0.00880	0.00048
2410	SiO ₂	0.00704	0.00027	0.0061
2860	Al ₂ O ₃	0.04400	0.00052	0.0041
Total		0.06336	0.00148	0.0153

The bad welding rod contained greater amount of oxides, especially Al_2O_3 , than the good welding rod.

Forging Steel—S.A.E. 1040 which gave some trouble on cutting had the following composition of gases and oxides:

Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Percentage of		
		Oxygen	Hydrogen	Nitrogen
1960	FeO	0.00107	0.00027
2140	MnO	0.00375	0.00027	0.0037
2410	SiO ₂	0.00428	0.00033
2860	Al ₂ O ₃	0.08770	0.00047	0.0084
Total		0.09680	0.00134	0.0121

On close examination the predominating inclusion consisted of Al_2O_3 .

The oxygen occurring as SiO_2 and Al_2O_3 may be responsible for difficulty in machining heat 58.

Pieces Per Tool Grind versus Type of Oxide in Steels of Same Chemical Analysis

Heat 61—65 Pieces Per Tool Grind				
Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Percentage of		
		Oxygen	Hydrogen	Nitrogen
1960	FeO	0.00145	0.00018
2140	MnO	0.00182	0.00009	0.0038
2410	SiO ₂	0.00145	0.00018	0.0006
2900	Al ₂ O ₃	0.00435	0.0057
Total		0.00907	0.00045	0.0101
Heat 58—30 Pieces Per Tool Grind				
1960	FeO	0.00168	0.00735
2140	MnO	0.00126	0.00016
2410	SiO ₂	0.00504	0.00016
2900	Al ₂ O ₃	0.00924	0.00026	0.00735
Total		0.01722	0.00058	0.0147

Spring Steels—As an example of difference in inherent characteristics we have two spring steels of similar composition, treated in the same manner but in a destruction test one steel "B" surpassed by far the other steel "A."

The results shown in the following table indicate that steel "A" contained considerably greater amount of gases and oxides than steel "B."

Vacuum Extraction of Gases and Oxides Occurring in Two Spring Steels

Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Steel "A"			Steel "B"		
		% O ₂	% H ₂	% N ₂	% O ₂	% H ₂	% N ₂
1960	FeO	0.00908	0.000936	0.00590	0.00259	0.000016
2140	MnO	0.01259	0.000855	0.00169	0.00246	0.00023
2410	SiO ₂	0.01945	0.000842	0.00212	0.00621	0.000016
2760	Aluminum Silicate	0.02404	0.000536	0.00853	0.01200	0.000143	0.00245
3000	Al ₂ O ₃	0.03060	0.000324	0.00908	0.01030	0.000115	0.00338
Total		0.09576	0.004293	0.02732	0.03356	0.000290	0.00606
Chemical Analysis:		Aluminum			0.019		
		Alumina			0.016		
					0.079		
					0.019		

For the temperature reduction of Al₂O₃ a range from 2860 to 3000 degrees Fahr. is used, depending upon the size of the Al₂O₃ particles. If the Al₂O₃ particles are fine, a complete reduction can be obtained at 2860 degrees Fahr. Then the temperature is raised to 3000 degrees Fahr. and if there is no more evolution of gases, a complete reduction of Al₂O₃ is considered at 2860 degrees Fahr.

Variation in the steel-making process is apparently responsible for the difference in performance of these two steels as is shown by the amounts of oxides in each steel.

Hardening Steels—Two steels of similar chemical analysis and treatment—on hardening one was deep and the other shallow hardened, yet no routine test could show the reason for such difference.

Fractional vacuum extraction of oxides differentiates between the type of oxides causing such variation.

Deep Hardening Steel				
Temp. of Extraction Deg. Fahr.	Probable Oxides Reduced	Percentage of		
		Oxygen	Hydrogen	Nitrogen
1960	FeO	0.00163	0.00047	0.00095
2140	MnO	0.00109	0.0019
2410	SiO ₂	0.00163	0.00020	0.00855
2860	Al ₂ O ₃	0.00217	0.00013	0.0019
Total		0.00652	0.00080	0.0133
Shallow Hardening Steel				
1960	FeO	0.00054	0.00020	0.00185
2140	MnO	0.00107	0.00027	0.0028
2410	SiO ₂	0.00160	0.00033	0.00374
2860	Al ₂ O ₃	0.00375	0.00027	0.00374
Total		0.00696	0.00107	0.01215

There seems to be an indication that the oxygen as FeO affects deep hardening.

Distribution of Total Oxygen and Gases in Ingot Sections and from Ingot to Ingot of a Heat				
Heat 235				
Ingot and Section		Percentage of, Total		
		Oxygen	Hydrogen	Nitrogen
No. 1 Ingot	Top	0.00825	0.00085	0.0066
No. 1 Ingot	Bottom	0.02508	0.00050	0.0116
No. 8 Ingot	Top	0.00238	0.00035	0.0062
No. 8 Ingot	Bottom	0.03052	0.00243	0.0146
Heat 188				
No. 1 Ingot		0.00156	0.00031	0.0036
No. 21 Ingot		0.00381	0.00045	0.0067
No. 42 Ingot		0.00768	0.00020	0.0048

Another group of steels showed the following results in samples of 4 inch x 4 inch size.

No.	Electric	% O ₂	% H ₂	% N ₂	% Al	% Al ₂ O ₃
No. 76		0.2815	0.00343	0.010	0.021	0.053
No. 96	O. H.—Outside	0.1015	0.00086	0.0127	0.037	0.024
No. 96	O. H.—Center	0.1136	0.00068	0.0130	0.030	0.014
No. 700	O. H.—Outside	0.0354	0.00193	0.0177	0.033	0.024
No. 700	O. H.—Center	0.0496	0.00122	0.0123	0.031	0.012

The important point we have here is an indication of the distribution of inclusions in the ingot and consequently in the billet. In this particular case, electric steel is higher in oxides and gases than the open-hearth steels.

In studying the distribution of gases and oxides throughout the

ingot, we find that oxides segregate toward the center, and that concentration of gases, hydrogen and nitrogen is higher in the outside of sections of the ingot. Metallic aluminum and alumina in steel have been determined by the method of analysis (*Iron Age*, Dec. 26, 1935, p. 23).

The above results illustrate a few of the numerous cases of steel-making problems which are answered to a closer degree than by other methods of investigation. This indicates a strong point for establishing such control for steel-making process.

ACKNOWLEDGMENT

The equipment used in obtaining the results given in this paper was set up according to the basic principles outlined in the paper by L. Reeve,¹² in which the method and the apparatus used for research work on welds are described in complete detail.

I owe a great debt of gratitude to Dr. S. L. Hoyt, director of metallurgy, and to Mr. M. A. Scheil, research metallurgist, A. O. Smith Corp., Milwaukee, for their gracious courtesy extended, enabling the author to witness the operation of their apparatus as well as the helpful co-operation given when we started the operation of our equipment.

DISCUSSION

Written Discussion: By John Juppenlatz, metallurgist, Treadwell Engineering Company, Easton, Pa.

Mr. Motok deserves considerable credit for his methods of extraction of gases from steels and their value in connection with the determination of elements of the unusual order which have a definite relationship to the quality of steel.

It seems as though we have a fair understanding of oxygen in steel and the methods used of ridding a bath of molten steel of its excess, but knowledge of hydrogen and nitrogen seems quite vague. An important finding of Mr. Motok's is that of the distribution of gases, the hydrogen and nitrogen content being highest on the outside of the ingot, while the oxides have segregated toward the center. Does this not mean that the hydrogen and nitrogen in the liquid metal have been greatly trapped upon rapid solidification and upon slower cooling, liberated to the center, finally finding exit through the pipe or shrinkage cavity? If this is true, would not the amount of shrinkage be a function of the amount of dissolved gases in liquid steel and the rate of solidification?

Hydrogen, when expressed in percentages of 0.001 seems relatively small, however, one volume of hydrogen compared with one volume of steel represents figures of considerable magnitude, suggesting the presence of hydrides

in molten steel which dissociate upon solidification. Further studies along the reasoning Mr. Motok has advanced should reveal some of the reasons for variations from heat to heat, heretofore unsolved.

It would be of interest to know if Mr. Motok has made further comparisons of gas content of electric and open-hearth steel. The figures shown indicate considerably higher hydrogen and oxygen contents of the electric steel. Is this condition typical of electric steel?

Written Discussion: By J. G. Thompson and H. C. Vacher, National Bureau of Standards, Washington, D. C.

This is the second paper to be published on the fractional vacuum fusion method; its predecessor was the original description of apparatus and procedure by Lewis J. Reeve in 1933.¹ It is hoped that additional evidence on the fractional vacuum fusion method will be forthcoming to demonstrate the reproducibility of results in the hands of different operators and further to demonstrate, by comparison with the values obtained by other methods of analysis, that the results obtained are what they are supposed to be. Reeve presented some evidence that FeO was reduced below 1100 degrees Cent. (2010 degrees Fahr.), MnO below 1200 degrees Cent. (2190 degrees Fahr.), SiO₂ at 1300 degrees Cent. (2370 degrees Fahr.), and Al₂O₃ at 1570 degrees Cent. (2860 degrees Fahr.). In the international project of co-operative analysis, which was reported at the February 1937 meeting of the A. I. M. E., Scheil's determinations by the fractional vacuum fusion method are reasonable values in comparison with those obtained by other methods of analysis. However, further data are needed to demonstrate the accuracy of the fractional separations and the reproducibility of results in the hands of different operators. The significance of the fractions in the determinations of hydrogen and nitrogen has not been satisfactorily explained.

The implication in the present paper, that the method is accurate to the fifth decimal place and to four significant figures in the determination of oxygen, particularly in dealing with a sample whose total volume may be as small as 0.2 cubic centimeters, should be supported by a more detailed description of the apparatus and technique. It is common practice to report small amounts of oxygen or nitrogen to the nearest 0.001 per cent and to report larger amounts to only two significant figures. This is likewise true for careful chemical analysis in general. Even in the determination of common elements, for which the methods of analysis have been thoroughly investigated and carefully standardized, 0.001 per cent is the usual limit. The determination of hydrogen is an exception; the low molecular weight and density of this element in comparison with oxygen and nitrogen permit its determination in correspondingly smaller amounts.

Minor points in the paper that invite discussion are as follows: The values reported for oxygen and alumina in Heats 73 and 60 (page 477) are unusually high for high carbon steels. There is a great difference between the Al₂O₃ content of spring steel "A" (page 478) as determined by the vacuum fusion method and by chemical analysis. According to the determinations of Al₂O₃ and aluminum silicate, by the vacuum fusion method, the alumina con-

¹L. J. Reeve, *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 113, Iron and Steel Division, 1934, p. 82-110.

tent of steel "A" is approximately 0.08 per cent. The determination of oxygen in aluminum silicate, as a separate fraction, is interesting. This is the first report of values for this constituent.

The correlation of the fractional vacuum fusion data with the properties and behavior of the steels indicates the usefulness of the method as a control method although further evidence is needed to establish its accuracy.

Written Discussion: By N. A. Ziegler, research engineer, Crane Co., Chicago.

For some time I have been sharing the opinion that most if not all of the peculiarities of steels, which Mr. Motok refers to as "inborn properties," and the reasons of which are not yet fully understood, could be explained on the strength of two observations: (1) a sufficiently complete, precise and accurate chemical analysis, of which analysis of gaseous constituents is only a part, and (2) state of subdivision of "nonmetallic" inclusions or particles which originate from the manufacturing practice, but do not react with the metal in the solid state and, consequently, do not change their state, size or form, unless deformed by mechanical working. It is, therefore, a great pleasure to see this paper by Mr. Motok, which at least partially confirms this idea.

I have been working for several years on the problem of gases in metals, and for this reason can fully appreciate the difficulties which a man thus engaged has to overcome in order to achieve results, and which Mr. Motok so modestly underestimates. I would like to ask the author the following few questions regarding his analytical method and procedure:

(1) It is particularly impressive to see the numerical results of the analysis, which the author presents down to the fifth and sometimes sixth decimal figure. In my method of gas analysis² the fourth decimal figure was about the limit of accuracy, and the author should be highly complimented for developing his method to such a high degree of refinement. It certainly would be interesting to know more about this method of gas analysis than Mr. Motok cares to state in his paper.

(2) It has been found that one of the principle sources of error in this kind of work comes from the contact of hot graphite crucible with the oxide refractory. In my method this difficulty has been solved by mounting the crucibles on a graphite rod, which in turn was mounted in the narrowed bottom end of the silica tube, outside of the high frequency coil, which for this reason never got hot. It would be interesting to know how Mr. Motok mounts his crucibles in the furnace.

(3) What is the advantage of introducing into the crucible, prior to the sample, a low melting alloy? In my work I never could find any benefit from doing that.

(4) Does Mr. Motok experience any difficulties in temperature reading, from a thin film of evaporated metal precipitating on the inside surface of the glass cover of his furnace? This is a usual occurrence when metals are being melted under a high vacuum, and I have found that readings of an optical pyrometer in cases like this are unreliable. I was compelled to control temperature by power input, which was calibrated against temperatures of an

²N. A. Ziegler, "Improved Method for the Analysis of Gaseous Constituents in Metals," *Transactions, American Electrochemical Society*, Vol. LXII, 1932, p. 175.

empty crucible, and had to be checked from time to time. In conclusion I would like to compliment Mr. Motok for a very interesting piece of work.

Written Discussion: By M. A. Scheil, research metallurgist, A. O. Smith Corporation, Milwaukee.

In reading over this paper it appears to the writer that the author has taken too much for granted and has presented his results and conclusions too briefly. There is very wide interest in work of this kind both here and abroad since the publication and discussion of the original work on the fractional vacuum fusion method, for the determination of gases in metals, by Dr. L. Reeve. I believe the author will welcome a discussion of his paper to bring out some of the details which are entirely missing.

We have been using the method of fractional vacuum fusion analysis, for the determination of gases in metals, since 1932. At first we were not certain that FeO and MnO could be determined separately and Dr. Reeve would report the FeO and MnO fractions together with a statement to the effect that FeO or MnO predominated or that FeO was present only in traces. This was determined by the rate of decomposition of the two oxides. If FeO was present a rapid gas evolution took place at 1050 degrees Cent. (1920 degrees Fahr.) and the gases were collected until the base pressure was established. This is the pressure in mm. of mercury of the empty graphite crucible.

Then the temperature was raised to 1150 degrees Cent. (2100 degrees Fahr.) and if a further gas evolution was noted, by a distinct and long rise in pressure, then this was collected and called MnO. When small volumes, less than 0.10 cc, of the first fraction at 1050 degrees Cent. (1920 degrees Fahr.) was collected, this was combined with the second fraction and the total gases analyzed were calculated as MnO at 1150 degrees Cent. (2100 degrees Fahr.). This matter of separating FeO and MnO has always been a matter of fine technique requiring close temperature control and frequent careful pressure readings. Samples high in FeO are particularly difficult to handle especially if the sample is large and the FeO inclusions are massive.

One of the first outside organizations to set up vacuum fusion equipment for fractional work was the author's company. Naturally, we were very interested in this activity because it meant that the method would be tried by others and we have co-operated with Mr. Motok in several instances during the installation of this equipment.

After the author had set up his equipment he requested that we send him some standard samples that could be used to check on the technique and reliability of his apparatus. We did not have standard samples to send to Mr. Motok but did send him some duplicate samples which we had already analyzed. These are not to be considered as a standard in the same category as a sample one would expect from the Bureau of Standards, but were simply adjacent bars selected from material available at the time. Some time later we were pleased to learn from the author his results on three of these samples. It appears that these three samples are published in Table I to point out the usefulness of this equipment. At this time, I should like to record the analyses that we made originally on these samples in order to show the similarity of results that can be obtained from the method of fractional vacuum fusion in the hands of different investigators.

A. O. Smith values are given on the left hand side of the data, and values reported to us by Mr. Motok on the right hand side.

No. 1 Semi-Rimming Plate									
A. O. SMITH ANALYSIS					REPUBLIC STEEL CORP. ANALYSIS				
C—0.22 Per Cent, Mn—0.60 Per Cent, Si—0.02 Per Cent									
Fraction at									
Degrees		Weight Per Cent			Degrees Cent.		Per Cent		
Cent.	Oxide	O ₂	H ₂	N ₂	Degrees Cent.	O ₂	H ₂	N ₂	
1050	FeO	0.0004	0.003	1070	0.00024	0.001	
1170	MnO	0.009	0.0004	0.003	1170	0.010	0.002	
1320	SiO ₂	0.011	0.0001	0.001	1320	0.011	0.00008	0.001	
1570	Al ₂ O ₃	0.003	0.0001	0.001	1570	0.006	0.00016	0.001	
TOTAL		0.023	0.0006	0.005			0.027	0.00048	0.005
Ordinary vacuum fusion									
0.020 Per Cent O ₂ —0.002 Per Cent N ₂									
No. 2 Shielded Arc Deposit									
C—0.08 Per Cent, Mn—0.55 Per Cent, Si—0.23 Per Cent									
Fraction at									
Degrees		Weight Per Cent			Degrees Cent.		Per Cent		
Cent.	Oxide	O ₂	H ₂	N ₂	Degrees Cent.	O ₂	H ₂	N ₂	
1050	FeO	0.0007	0.000	1070	0.001	0.00014	
1170	MnO	0.010	0.0007	0.000	1170	0.017	0.00014	
1320	SiO ₂	0.052	0.0007	0.005	1320	0.052	0.00056	0.005	
1570	Al ₂ O ₃	0.008	0.0000	0.004	1570	0.007	0.001	
TOTAL		0.070	0.0014	0.009			0.077	0.00084	0.006
Ordinary vacuum fusion									
0.079 Per Cent O ₂ —0.010 Per Cent N ₂									
No. 3 Bare Weld Metal									
C—0.02 Per Cent, Mn—0.09 Per Cent, Si—0.010 Per Cent									
Fraction at									
Degrees		Weight Per Cent			Degrees Cent.		Per Cent		
Cent.	Oxide	O ₂	H ₂	N ₂	Degrees Cent.	O ₂	H ₂	N ₂	
1050	FeO	0.282	0.00014	0.160	1070	0.032	0.00057	0.097	
1170	MnO	Trace	1170	0.240	0.00014	0.053	
1320	SiO ₂	0.000	0.0000	0.010	1320	0.009	0.00036	0.039	
1570	Al ₂ O ₃	0.016	0.0000	0.002	1570	0.027	0.001	
TOTAL		0.298	0.0001	0.172			0.308	0.0011	0.190
Ordinary vacuum fusion									
0.304 Per Cent O ₂ —0.181 Per Cent N ₂									

There is good agreement between the total oxygen and nitrogen values as determined by the ordinary vacuum fusion method and the sum of the separately determined fractions from the fractional method. This agreement stamps the fractional method as a rational procedure. We could cite other data on selected steels, more homogeneous than weld metal, which would bring out even more so the excellent agreement on total oxygen for the fractional procedure with the accepted method of total oxygen by the ordinary vacuum fusion.

Mr. Motok's results on samples No. 1 and No. 2 in Table I are in good agreement with our reported results shown in the prepared table for oxygen, nitrogen and hydrogen. No. 3 sample of Bare Weld Metal agrees well for total oxygen and nitrogen considering that variations in oxygen and nitrogen are expected in the different welded layers of this material. The separation of the first two oxide fractions is decidedly at variance with our results. The high oxygen as MnO that Mr. Motok reports could not possibly occur since there is not sufficient manganese present in this metal to account for his reported value even if it were oxidized 100 per cent. The oxygen as FeO is decidedly too low for this type of weld metal. I would refer the author to a

paper by Dr. S. L. Hoyt³ for a complete discussion of the metallurgical nature of these two different weld metals. Dr. Hoyt's paper discusses the occurrence of oxygen in weld metal from the metallurgical interpretation of fractional oxygen determinations, microscopic examination of foreign inclusions, and metallurgical characteristics such as: McQuaid-Ehn test, hot shortness tests, deep etch and sulphur print tests, strain and quench aging tests. These tests are necessary to properly interpret the results obtained from the fractional oxygen values and certainly should be considered when evaluating the quality of materials.

The fractional method, as shown by the examples cited by the author, is very critical in determining small amounts of oxides and gases. However, I do not believe the method is refined enough to warrant reporting oxygen or nitrogen to five places after the decimal point. I would be strongly inclined to doubt that a check analysis could be obtained closer than one point in the third place from adjacent samples in the same piece of steel.

It would appear that the example cited for deep versus shallow hardening steel is splitting hairs. There is less than 0.002 per cent oxygen as alumina difference between these two steels. I should like to ask the author how many check analyses he has made on these two steels to verify this slight difference and his conclusions that 0.004 per cent oxygen as alumina in this particular grade of steel prevents deep hardening.

Interpretation of fractional oxygen values is not conclusive by itself, it requires a microscopic study to point out the state of aggregation of these separately determined oxides which rarely occur singularly as such in the sample, as well as the size and distribution of the inclusions. As an example of this, I would cite the author's values for two high carbon steel with good and poor impact. Quite logically one could expect differences in notch toughness from two steels varying so widely in alumina. How much of this difference though is due to possible segregation or particle size and distribution? It should be pointed out that the fractional method does differentiate between the different oxides but does not distinguish their aggregation or particle size.

Along with the gas analyses the author should report the usual chemical analyses. This would indicate how the steel was deoxidized (whether manganese or silicon-killed). Also, we should know if the deoxidizers were added to the furnace or to the ladle. This is especially important since the author has reported aluminum silicate on four high carbon steels. We are extremely interested in the separate fraction that is reported as aluminum silicate. Particularly so, when the author makes the statement that if the alumina particles are fine, a complete reduction can be made at 2860 degrees Fahr. (1570 degrees Cent.). We would like to know how accurate this separation of aluminum silicate can be determined. Is the particle size important? Is the author able to separate aluminum silicate from furnace-killed steels as well as steels to which the final deoxidizers are added in the ladle?

There has been a suggestion in our work at A. O. Smith that some of the alumina in very fine dispersion reduces in the third fraction at 1320-1350 degrees Cent. (2410-2460 degrees Fahr.). This, however, is a very unusual oc-

³S. L. Hoyt, "Metallurgy of Arc Deposited Weld Metal," *TRANSACTIONS, American Society for Metals*, Vol. 23, 1935, p. 61.

currence in our experience and we should like to have the author's experimental evidence on which he bases his conclusions of an aluminum silicate fraction. This is fundamental to the whole process of fractional vacuum fusion.

I believe the author should make some comments on the alumina analyses he has reported for steel A and steel B, two spring steels. Steel A is reported as having 0.031 per cent oxygen as alumina or 0.066 per cent calculated alumina by fractional vacuum fusion. By chemical analysis the alumina is reported as 0.016 per cent. Steel B is reported as 0.010 per cent oxygen as alumina or 0.021 per cent calculated alumina by fractional vacuum fusion. By chemical analysis the alumina is reported as 0.019 per cent. The chemical analysis for alumina on steel B agrees well with the author's fractional vacuum fusion analysis, but shows a large difference for steel A. I should like to know what explanation the author has for this variation in the alumina content between the two methods for steel A. Also, does the presence of aluminum silicate interfere with the analysis of alumina in the chemical method the author refers to.

The author has mentioned the use of tin, added to the graphite crucible after outgassing and dropping the temperature, to melt the steel. At what temperature does the author observe complete melting of his steel sample? Has the author used any other metal to lower the melting point of his steel sample for fractional vacuum fusion? The author mentions the use of this equipment for double check fractional extraction. What provision has he made for reading the temperatures optically through the quartz window after the first extraction? I ask this because tin is annoying in this respect. It begins to boil in vacuo at about 1350 degrees Cent. (2460 degrees Fahr.) and condenses upon the cooler portions of the vacuum tube and window. I should like to inquire what provisions the author has made to take care of this problem when he makes check runs supposedly in the same set-up.

One rather broad statement in paragraph two of the abstract to this paper would lead others to believe that rimming steel as a class contains high oxygen as FeO and alumina. This statement could apply to a particular grade of rimming steel. Rimming steel as used for deep-drawing may contain almost negligible amounts of these two oxides. A typical analysis of good forming sheet is:

Frame Stock 0.10 per cent Carbon—Sheet 0.156 inch thick, 0.023 inch rim, 0.110 inch core.

		0.40 Per Cent Mn, 0.01 Per Cent Si 100 Per Cent Rim		
Fraction at Degrees Cent.	Oxide	O ₂	N ₂	H ₂
1150	FeO	0.001	0.001	0.00003
1170	MnO	0.008	0.003	0.00003
1320	SiO ₂	0.002	0.000	0.00000
1570	Al ₂ O ₃	0.003	0.000	0.00000
TOTAL		0.014	0.004	0.00006
		Cross Section—29 Per Cent Rim Included		
Fraction at Degrees Cent.	Oxide	O ₂	N ₂	H ₂
1050	FeO	0.001	0.001	0.00015
1170	MnO	0.015	0.003	0.00000
1320	SiO ₂	0.004	0.000	0.00000
1570	Al ₂ O ₃	0.001	0.000	0.00000
TOTAL		0.021	0.004	0.00015

Another problem in all vacuum fusion analyses is the determination of dissolved CO and CO₂ gases present in the steel. I should like to ask the author if he has considered this point and has arrived at any method for separating the dissolved CO gas, that might be liberated from his sample of rimming steel, from the reaction CO gas obtained by the reduction of FeO at 1070 degrees Cent. (1960 degrees Fahr.).

These remarks are offered by one who has worked with the method as first proposed by Dr. L. J. Reeve and are given in the spirit of research and not as a criticism of the author's paper.

Written Discussion: By John Chipman, American Rolling Mill Co., Middletown, Ohio.

This latest contribution to the development of methods for the study of gaseous elements in steel makes up in breadth of outlook what it lacks in clarity of detail. The author attempts to cover the entire field of gases and nonmetallic inclusions, with the result that very little space is left for the presentation of the method of analysis and the results obtained. His avoidance of any discussion of those vital features of his analytical method, without which it is impossible to appraise its dependability, will doubtless inspire a certain amount of incredulity among those who have wrestled with the difficulties of high temperature vacuum technique.

In considering the results of a given method of investigation and its application to steel-making, it is necessary to differentiate between criticism of the method itself and the less important and more specific objections which may be brought against a single set of results obtained by a single experimenter. The vacuum fusion method, properly carried out, is perhaps the only dependable method for determining total oxygen in steel. The fractional modification of this method yields a much greater amount of information, and any skepticism as to whether a given fraction actually corresponds to a certain oxide need not interfere with an appreciation of the potentialities of the method.

There are a number of well-known conditions which must be met in designing equipment for work of this kind, and in conducting the analytical determinations. Inspection of the diagram and photographs shows that some of these have been overlooked. The tube connecting the furnace and the pump should be short, wide, and free from constrictions. The McLeod gage should be connected near the furnace if any significance is to be attached to its indications. The high vacuum obtainable before heating the crucible is a useful precaution against leakage, but is no assurance that the blank is small. The author omits the more important data on the degree of vacuum obtainable when the crucible is hot. No apparatus has yet been devised in which the blank need not be considered. In fact, a graphite crucible continues to evolve gases, especially carbon monoxide and hydrogen, even after prolonged heating at higher temperatures than that at which Mr. Motok prepares his crucible. The method of mounting the graphite crucible inside the furnace tube has a very important bearing upon the size of the blank. Since this is not described, it is impossible to judge whether his results are subject to errors that other analysts have reported from this source.

It should be axiomatic that the whole is equal to the sum of its parts, and

we may, therefore, proceed to examine some of the results reported in terms of the total oxygen contents of several of the steels. In Heat 60, the author finds a total of 0.12341 per cent oxygen. This is a high carbon steel. Now, if this method is going to throw any light on quality steel-making, the reader would certainly be interested in knowing how such a steel was made. This would be abnormally high oxygen, even for open-hearth iron, but for high carbon steel it is unheard of. Some other features of the melting practice on this heat would be of interest. How do you go about it to get 0.09933 per cent oxygen in the form of Al_2O_3 into a high carbon heat? This would be 0.21 per cent Al_2O_3 . How do you pour a high carbon heat containing 0.002085 per cent hydrogen and 0.02525 nitrogen, and have it stay in the molds? or did it? The same question might be asked concerning the spring steel with 0.09576 per cent oxygen, 0.004293 per cent hydrogen, and 0.02732 per cent nitrogen. What kind of electric furnace practice results in an oxygen content of 0.2815 per cent? How do you get the nitrogen content of an open-hearth heat up to 0.0177 per cent? The simplest answer to such questions might be found in a misplaced decimal. Perhaps the blank correction is higher than the author supposes. Possibly there really are such steels. In either case one would like to protest against the author's habit of expressing results to the fifth decimal place.

Author's Closure

The interest in the subject treated in this paper is very much appreciated.

We cannot accept any credit as pioneers in developing a method or apparatus for the fractional extraction of gases in steel. In 1934, when we surveyed the research field for an acceptable and comparatively accurate method for determination of gases and oxides in steels, we decided that the method and the apparatus developed by Dr. L. J. Reeve, formerly of A. O. Smith Corporation, offered excellent possibilities for practical applications to steel making problems.

A description of Dr. Reeve's method and apparatus was published in *Transactions of A.I.M.E.*, Vol. 113, Iron and Steel Div., 1934, p. 82-110. The method and apparatus are very ably described by Dr. Reeve, and well discussed, thus bringing this method to the general knowledge of those interested in this field.

In our paper an attempt was made to indicate the applications of an equipment which was set up in our laboratory according to the principles developed by Dr. Reeve at A. O. Smith Corporation. We received considerable assistance from Dr. S. L. Hoyt, director of research; and M. L. Scheil, research metallurgist of the A. O. Smith Corporation, in setting up and operating our equipment.

Regarding Mr. Juppenlatz's discussion of this paper, his reasoning, that the amount of shrinkage could be a function of the amount of dissolved gases in liquid steel, might be explained by the difference in hydrogen solubility in iron at different temperatures as follows. At 350 degrees Cent. it is 0.00005 per cent by weight; at 850 degrees Cent., 0.00025 per cent; at 950 degrees Cent., 0.00045 per cent; at 1400 degrees Cent., 0.001 per cent; at 1500 degrees Cent.,

0.0012 per
0.0028 per

Accor
through

- (a)
- (b)
- (c)
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0.0012 per cent; at 1535 degrees Cent., 0.0024 per cent; at 1650 degrees Cent., 0.0028 per cent.⁴

According to the results obtained by Swinden and Stevenson⁵ passing gas through deoxidized iron and mild steel has the following effects:

- (a) Hydrogen—unsoundness.
- (b) Nitrogen—no unsoundness.
- (c) Hydrogen followed by nitrogen—no unsoundness.
- (d) Carbon monoxide—slight unsoundness.
- (e) Carbon dioxide—no unsoundness.

Since hydrogen produces unsoundness, this might suggest the presence of hydrides in molten steel, which dissociate upon solidification.

A representative comparison of the gas content could be obtained only on samples taken from the same location in the same ingot of a heat. In the examples given in table "Distribution of Total Oxygen and Gases in Ingot Sections and from Ingot to Ingot of a Heat," both heats represent same grade of steel, but heat 235 is electric steel and heat 188 is open-hearth steel. Aluminum silicate, as inclusion in steel, was also identified by the microscopic examination.

Some of the improvements in apparatus and in technique of operation enable us to obtain results practically free of blanks. Tin is added to the crucible prior to the sample in order that any gases which might occur in the tin may be extracted, thus eliminating any need for blank. A complete melting of the steel sample is obtained in the temperature range 2100 to 2200 degrees Fahr., depending on the amount of tin used.

Double check fractional extraction is obtained by making a run one day and another run the following day. This procedure helps to eliminate any error that might occur in the operation of the equipment at any time.

There is a difference of 30 inches from bottom of graphite crucible to the top of pyrex head and sample holder and thus we have not experienced any difficulty in reading temperatures, although we calibrated the power input per weight charge vs. temperature with and without the window. In regard to the solubility of CO in steel, the works of Dr. Styri,⁶ Dr. Kinzel,⁷ as well as the work of the committee on the Heterogeneity of Steel Ingots⁸ indicate that the solid solubility of CO in steel is very low, if any.

The results given in this paper were presented as obtained and as actually used in solving practical steel making problems and no attempt was made to prove any particular theoretical speculation. These results represent only a small fraction of the numerous results and their actual successful application.

Mr. Scheil's contribution points out a few of the details required in developing a technique for determination of the gases and oxides in steel and of the interpretation of the results obtained.

⁴H. Schenck, "Physikalische Chemie der Eisenhüttenprozesse," Vol. 1, p. 156.

⁵T. Swinden and W. W. Stevenson. Section VIII, "Some Experiments on Gases in Iron and Steel and Their Effect on the Solidification of Ingots," in the Sixth Report on the Heterogeneity of Steel Ingots (British Iron and Steel Institute, 1935, p. 137-150).

⁶H. Styri, "Theory and Practice of Steel Refining," *Journal, Iron and Steel Institute*, 1923, Vol. 108, p. 216.

⁷A. B. Kinzel and J. J. Egan, "Experimental Data on the Equilibrium of the System Iron Oxide-Carbon in Molten Iron," *A.I.M.E., Iron and Steel Division*, 1929, p. 302-319.

A STUDY OF THE EFFECT OF THE ALUMINUM ADDITION ON THE STRUCTURE OF A QUENCHED CARBON STEEL

By H. W. McQUAID

Abstract

In this paper the results of an attempt to indicate the effect of aluminum on the tendency to form heavier carbide particles have been shown. The subsequent effect of the carbide particle size and carbide structure on the hardenability and grain size is shown, together with a discussion of the results obtained.

It is reasoned that the difference in hardenability of heats of steel of the same analysis is due to variation in the amount of carbide in solution in the austenite as well as the distribution of the carbon in the individual austenite grain. It is shown that one of the effects of the addition of aluminum is to increase the thickening of the carbides at temperatures below the critical range. In a lamellar pearlitic steel the thickening of the carbide occurs at the edges of the carbide plates so that, while solution of the carbide occurs easily within the pearlite grain, there is considerable resistance to solution of the heavier carbide particles due to the thickening of the carbide at the border of the ferrite. It then requires either high temperature or greater time, or both, to obtain complete solution of the carbide at the ferrite boundaries. This reduces the effective hardness, tends to retain the ductility and resistance to impact and also interferes with the austenitic grain growth. It is believed that much of the grain growth phenomena, hardenability, Izod variation and variation in physical properties, can be explained by the effect of variation in carbide particle size. This variation in carbide particle size results in an unequal distribution of carbon in the austenite at the time of quenching from the center of the grain to the grain boundary. The extent of this unequal distribution, depending as it does not only upon the presence of certain elements in the ferrite but also upon previous heat treatment, it is argued, is one of the most important factors in the results obtained by the final heat treatment.

A paper presented before the Eighteenth Annual Convention of the American Society for Metals, Cleveland, October 19 to 23, 1936. The author, H. W. McQuaid, is metallurgist, Republic Steel Corp., Massillon, Ohio. Manuscript received June 25, 1936.

It is suggested that maximum hardenability in a steel of a given analysis is not primarily a function of grain size but of carbon solution. Thus it is possible that a coarse-grained steel will harden more deeply than a fine-grained steel, not because of any variation in the size of the grain but because of the distribution of the carbides in solution in the steel at the quenching temperature. A coarse-grained steel, it is thought, might be one in which we have a uniform and complete solution of carbon, in which the boundaries have been obliterated by carbon diffusion. The fine-grained steel on the other hand might be one in which either insufficient time or insufficient temperature, or both, has been available to permit full solution of the carbides together with complete diffusion of the dissolved carbon across the grain boundary.

Whether the effect of the aluminum on the carbide size and solubility is due to the formation of carbides containing aluminum or whether it is entirely due to the presence of aluminum in solution in the ferrite is not indicated, although it is believed that the effect on the carbide is due to the presence of the aluminum in the ferrite rather than the formation of a special carbide. That this would seem to be the case is reasoned from the fact that a similar effect can be produced by the presence of oxygen, probably in the form of FeO in solution in the ferrite. Apparently when no element which affects the carbide solubility is present, the solution is very rapid even when the carbides have been subjected to a long time of heating at temperatures just below the critical range.

THIS investigation is a continuation of work done in connection with the Campbell Memorial Lecture of 1935. In this lecture it was suggested that perhaps the presence of aluminum in solution had some effect on the solubility of carbide in austenite and that there was an increased tendency for the carbide particles to coalesce at temperatures just under the critical range in steels which contained in solution in the ferrite some elements such as aluminum. It was suggested that this effect on the carbide particle size affected the temperature of solution, the grain growth range and the formation of martensite. This, of course, was a rather bold suggestion in view of the fact that the action of insoluble nonmetallic oxides as the major factor in the control of grain size had received wide acceptance by some of our best known metallurgists.

It should be acknowledged here that the evidence presented regarding the effect of aluminum on the condition of the carbides might

in many ways be considered a continuation of the work done by R. G. Guthrie. In a paper, presented before the American Society for Steel Treating, at Chicago, September 1926, he discusses the effect of the condition of the cementite on the properties of the steel and presents a very interesting study of carbide structures in low carbon steel.

It should also be acknowledged here that the writer is deeply indebted to Miss Mary Norton, Watertown Arsenal, Watertown, Mass., for her fine work in preparing the unusual and very excellent photomicrographs upon which this paper is based. The writer is also indebted to Col. G. F. Jenks, Commanding Officer, Watertown Arsenal, for his co-operation in the preparation of the necessary photomicrographs.

We are also indebted to R. G. Guthrie and L. F. Lottier for the interest which they have shown in this work and the preparation of photomicrographs.

It is a well known fact to those who have made a study of the effect of carburizing temperatures on the case characteristics, that one of the effects of lowering the carburizing temperature is to increase the maximum carbon content of the hypereutectoid zone. It is often observed that a long time carburizing at temperatures of approximately 1500 degrees Fahr. (815 degrees Cent.) will result in the presence of spheroidal carbides at the surface in sufficient amount so that a chemical analysis of the first 0.005 inch of the surface will show a carbon content in excess of 3 per cent.

This is due to the fact that carbides are first formed at the surface, which must then be dissolved in the austenite to permit carbon diffusion into the steel. At low temperatures the rate of carbon diffusion is extremely slow, resulting in a saturated austenitic layer at the surface in which the carbide particles formed are difficultly soluble. By increasing the carburizing temperature, the diffusion rate of the carbon in the austenite increases so that the ability of the surface layers of the austenite to dissolve the surface carbide is increased. This results in a lower carbon concentration at the surface and the first 0.005 inch after a long 1600 degrees Fahr. (870 degrees Cent.) Carburizing will show a carbon content of approximately 2 per cent. If the temperature is further increased, the surface carbon decreases steadily till finally a point is reached, at very high temperatures, at which it is difficult to obtain any excess cementite. The same condition of difficult solubility occurs at higher temperatures

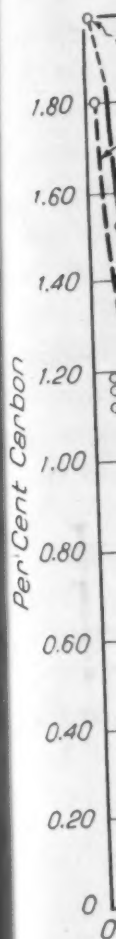


Fig. 1
Carburizing temperature on surface carbon content

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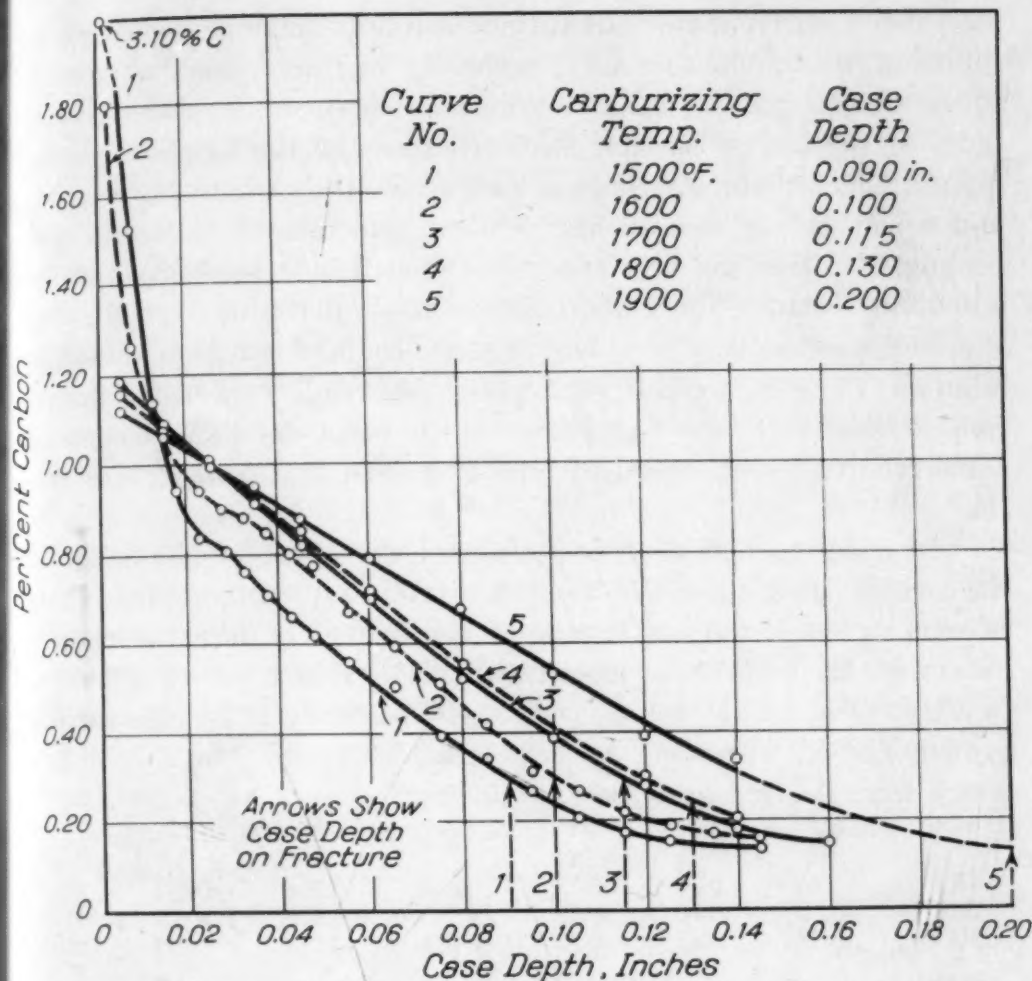


Fig. 1—Case Depth-Carbon Content Curve. Shows the Effect of Carburizing Temperature on Carbon Concentration. Test piece packed in Compound and Carburized at Temperatures given. (R. W. Schlumpf.)

in steels containing alloys such as vanadium, tungsten, etc., which form carbides which are more difficultly soluble.

The free carbides which are found at the surface after carburizing at temperatures of approximately 1500 degrees Fahr. (815 degrees Cent.) should present the same problem of solution as is found in the carbides beneath the surface. If the carbide is distributed in fine plates such as we find in lamellar pearlite, the solution is apparently almost instantaneously effected, whereas if the carbide occurs in larger, more coalesced masses, the solution is difficult and at ordinary heat treating temperatures very much slower than we have been led to believe.

It is apparent from microscopic study of carbide formations as they occur in various steels that we may have in the same piece of

steel many different rates of carbide solution ranging from the condition of maximum solubility, occurring in finely lamellar pearlite, to the slowest possible solution which would occur in spheroidal carbides of the largest possible size. In steels of the so-called normal type in which nothing is present to increase the carbide particle size, and which usually form a fine pearlitic structure on relatively slow cooling, we have the best conditions for carbide solubility and the minimum distance for carbon diffusion so that this type of steel should transform very quickly. In steels containing a high aluminum addition, there is, we believe, a maximum tendency for the formation of relatively heavy carbides, which resist solution and persist for a relatively long period of time at normal heat treating temperatures.

In order to obtain an indication of the effect of aluminum on the carbide particle size and the structure after quenching, three heats of steel were selected which were of approximately the same analysis except for the addition of aluminum, and these steels were submitted to a treatment which would magnify the tendency to carbide particle growth and its effect on the hardened structure. The three heats which were selected analyzed as follows:

Heat No.	C	Mn	Si	P	S	Al	Al ₂ O ₃
3B3	0.36	0.74	0.15	0.013	0.028	0.075	0.026
2B2	0.37	0.70	0.17	0.013	0.022	0.050	0.020
5B3	0.38	0.85	0.13	0.015	0.028	0.011	0.020

These heats were made from the same scrap charge, under the same slag composition; the principal difference in the heats being in the amount of aluminum added. Any controversy as to the aluminum analysis may be eliminated if we assume that the difference between the three heats consists primarily in the aluminum added, being approximately 8 ounces per ton in heat 5B3, 32 ounces per ton in heat 2B2 and 48 ounces per ton in heat 3B3. Samples for tests were rolled at the same time to 1½ inch diameter bars which were normalized at 1800 degrees Fahr. (980 degrees Cent.) one hour at temperature. One inch specimens were heated to 1225 degrees Fahr. (665 degrees Cent.) and held for 24 hours at this temperature. Samples were quenched directly from this temperature in water. Samples were also taken from the 1225 degrees Fahr. (665 degrees Cent.) temperature, transferred quickly to a furnace at 1500 degrees Fahr. (815 degrees Cent.) and held at temperature for 15 minutes. They were then quenched in water. Specimens were also transferred

from the 1225 degrees Fahr. (665 degrees Cent.) temperature quickly to a furnace at 1700 degrees Fahr. (930 degrees Cent.), held at temperature for 15 minutes and quenched in water. Studies of the structure, hardness, etc. were made on the specimens so treated.

The object of the long hold at 1225 degrees Fahr. (665 degrees Cent.) was to magnify the relative tendency of the carbide to form in larger masses at a temperature below the critical range. This treatment was used on the pearlitic or normalized structure rather than on the quenched structure, not only to simulate commercial practice but also to obtain maximum grain boundary effect rather than spheroidization within the pearlitic grains. The specimens were transferred to furnaces at 1500 and 1700 degrees Fahr. (815-930 degrees Cent.) to obtain some indication of the rate of solution and the effect of the structure before heating to the critical range, on the structure obtained by quenching from above the critical temperature. Thus it was expected to develop an indication of the effect of the aluminum on the carbide structure of a hypoeutectoid steel having the carbide in the form of lamellar pearlite and the relation of this carbide structure to the rate of solution and the final structure obtained on quenching.

The results obtained indicate a rather marked contrast between the three different heats of steel. Figs. 2 to 11 indicate the structures obtained after the 24-hour holding at 1225 degrees Fahr. (665 degrees Cent.) following by a water quench. It is interesting to note the apparently great difference in the amount of ferrite in these three heats and conversely the great difference in the apparent amount of the pearlite present. To the ordinary observer there would seem to be a much greater percentage of carbon in heat 5B3, Fig. 4, than there is in the other two heats. In order to remove any doubt as to the carbon content, check drillings adjacent to the micro sections were analyzed for carbon, showing that the carbon content was practically identical in all three pieces. It is reasonable to suppose, therefore, that since there is such a marked difference in the apparent amount of pearlite in these heats that the steel containing the high aluminum addition must have a pearlite which contains a higher maximum carbon in the pearlite grains than the heats with the lower aluminum addition. This is supported by the findings of Dr. Reed¹ who showed that one of the effects of aluminum is to increase the carbon con-

¹E. L. Reed, "Influence of Special Elements on the Carbon Content of the Iron-Carbon Eutectoid," *TRANSACTIONS, American Society for Steel Treating*, Vol. 20, 1932, p. 115.

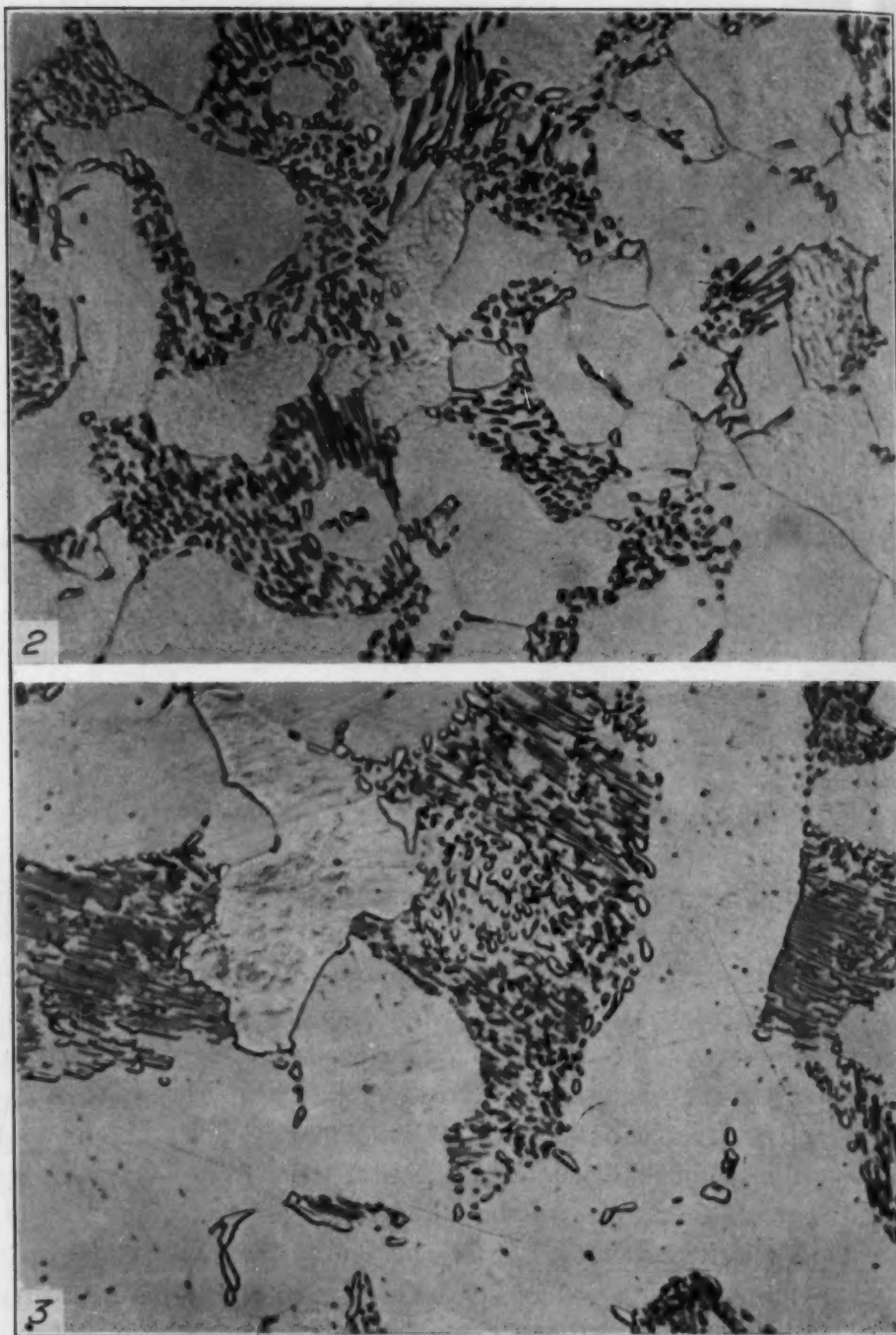


Fig. 2—Heat 3B3. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) and Water-Quenched. 1000 Diameters, Nital Etch. (Miss Norton.)

Fig. 3—Heat 2B2. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) and Water-Quenched. 1000 Diameters, Nital Etch. (Miss Norton.)

tent of the eutectoid. It would seem plausible to believe that the apparently greater amount of pearlite in the lower aluminum steel is due to a much smaller average carbide particle size, although this may

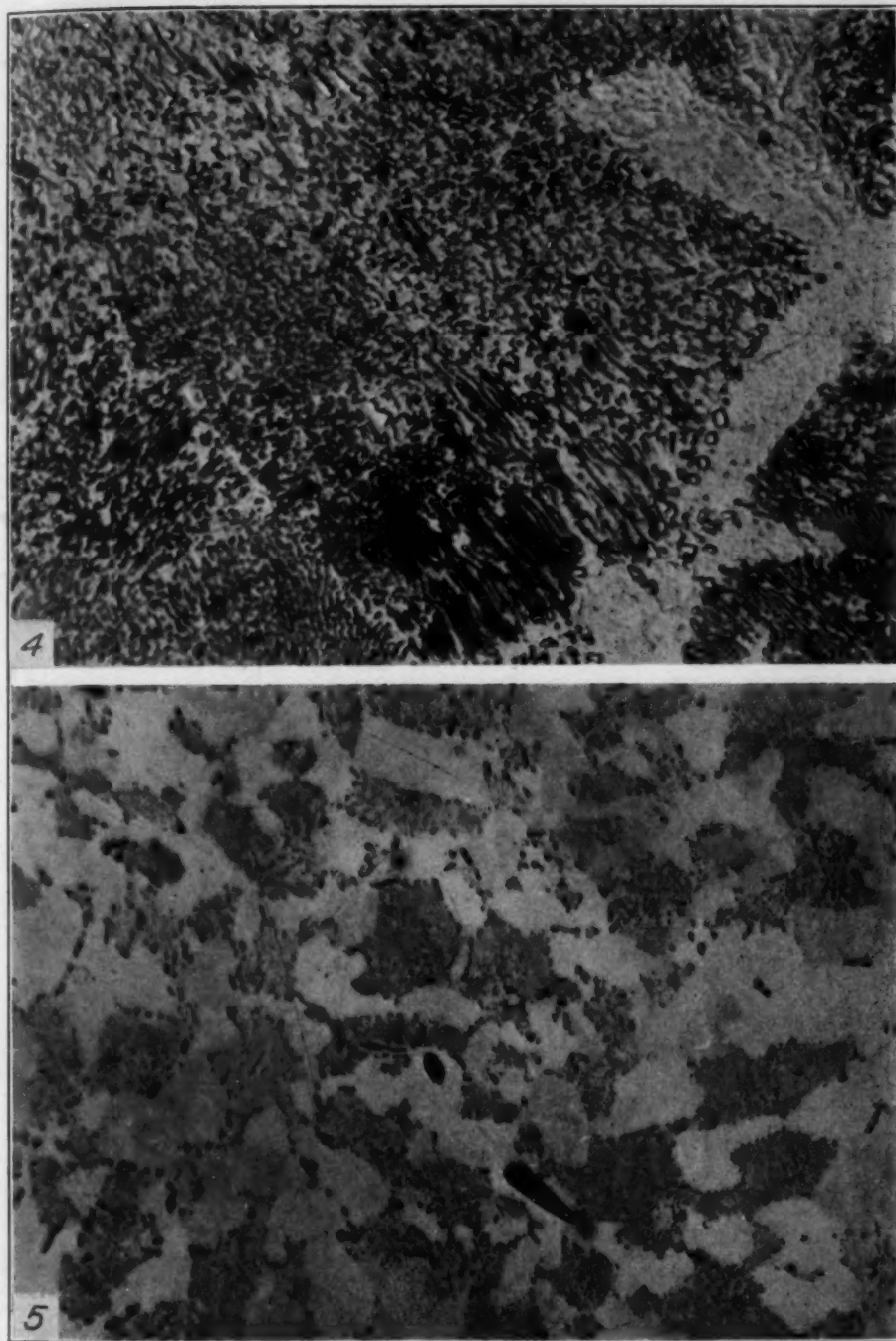


Fig. 4—Heat 5B3. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) and Water-Quenched. 1000 Diameters, Nital Etch. Note the Apparent Difference in the Amount of Carbide and Ferrite Present in Figs. 2, 3 and 4. (Miss Norton.)

Fig. 5—Heat 3B3. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) Followed by Water Quench. 450 Diameters, Sodium Picrate Etch. (Miss Norton.)

not be necessarily true if a different type of carbide is formed in the presence of aluminum. At least the apparent result of adding the aluminum to this type of steel is to increase the amount of free fer-

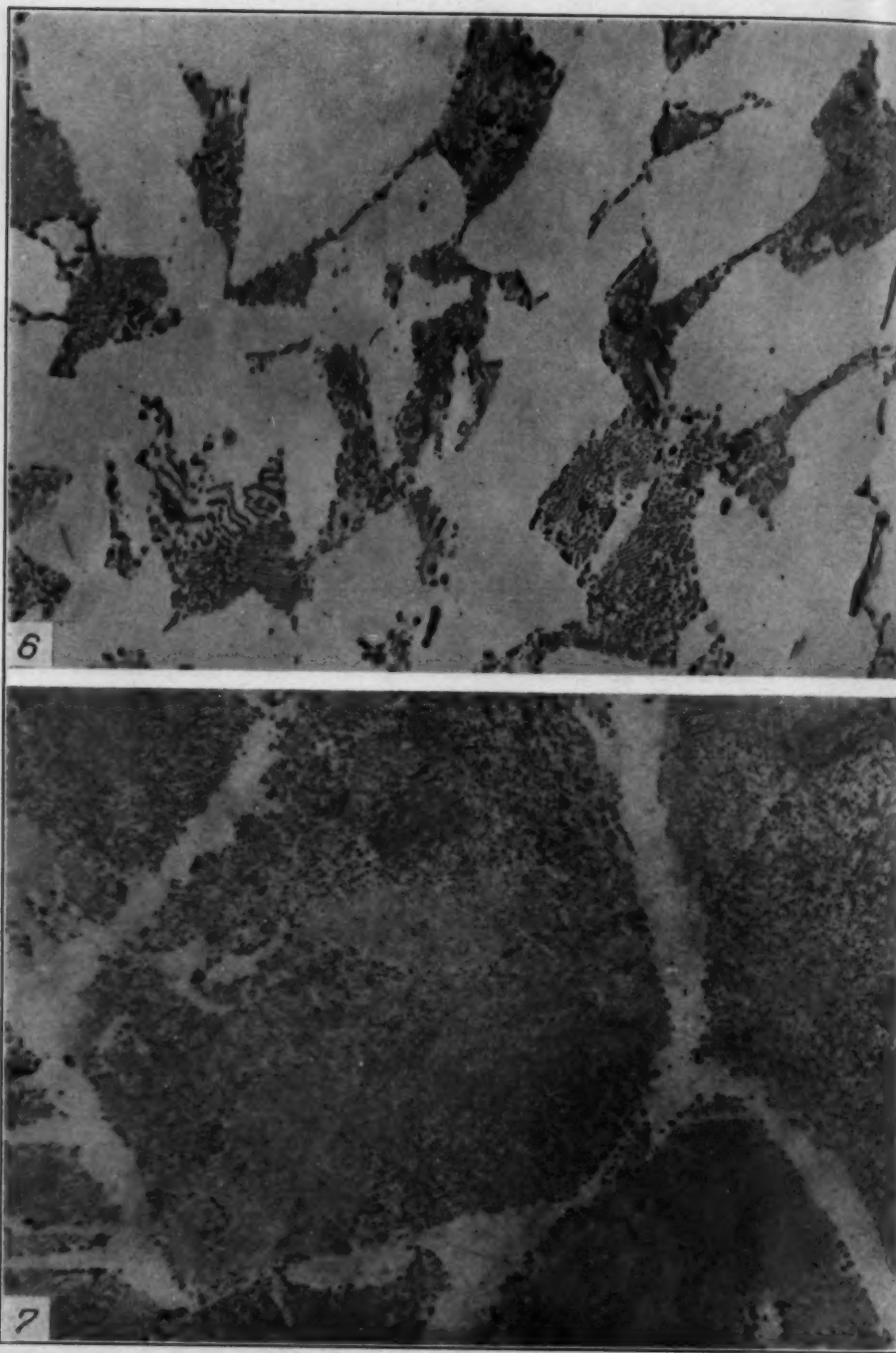


Fig. 6—Heat 2B2. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) Followed by Water Quench. 450 Diameters, Sodium Picrate Etch. (Miss Norton.)

Fig. 7—Heat 5B3. Structure After 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.) Followed by Water Quench. 450 Diameters, Sodium Picrate Etch. Note the Heavier Carbide particles Outlining the Pearlite Grains. (Miss Norton).

rite and to decrease the apparent amount of pearlite. Figs. 5 to 11, inclusive, show the structures developed in the same steels by a sodium picrate etching. These present a very interesting indication of

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what is apparently happening to the carbide when held for a sufficient length of time at a temperature close to the critical range. The heavy carbide particles which have developed adjacent to the ferrite are clearly evident. Apparently the tendency towards heavy coalesced carbide is very much greater in the steels in which the aluminum addition has been high as compared to those in which the aluminum addition has been relatively small. This is, indeed, a significant difference since it is evident that the larger ferrite boundary is due to thickening of the carbide which had existed at one time in the form of thin plates. It immediately becomes evident that in order to obtain a complete solution of the carbide in the boundary austenite after heating above the critical that these heavy carbide particles must go into solution and the carbon diffuse completely across the original ferrite areas.

Apparently then, one of the primary effects of the aluminum-addition on steels heated at temperatures just below the critical range is to cause a retraction of the carbide from the boundary ferrite, thereby forming a larger ferrite mass free from carbon and also much heavier carbide at the pearlite boundaries. This would require then for the formation of a complete and uniform carbon distribution in the austenite that either the high aluminum steel be heated to a higher temperature than the lower aluminum steels or that they be held for a much longer time at ordinary temperatures. Not only is the solubility of the carbide reduced but due to the larger ferrite masses, it becomes necessary for the diffusion of the carbon to proceed for a longer time in order to obtain carbon diffusion to the extreme austenitic grain boundary itself.

The rate of diffusion of the carbon through the austenite at the grain boundaries is of considerable importance in determining the structure which will be obtained on quenching.

It is evident that diffusion of the carbon cannot proceed until carbide solution in the austenite has been effected. At the temperatures usually employed for hardening commercial steels by quenching, the diffusion rate of carbon in the austenite is extremely slow, although because of the small distances usually required for the diffusion, the time element is in most steels within commercial limits. It is believed, moreover, that variation in diffusion rates between steels of various types is not especially great, although it is well known that the addition of some elements such as silicon and nickel will decrease the rate of diffusion considerably. Extensive tests

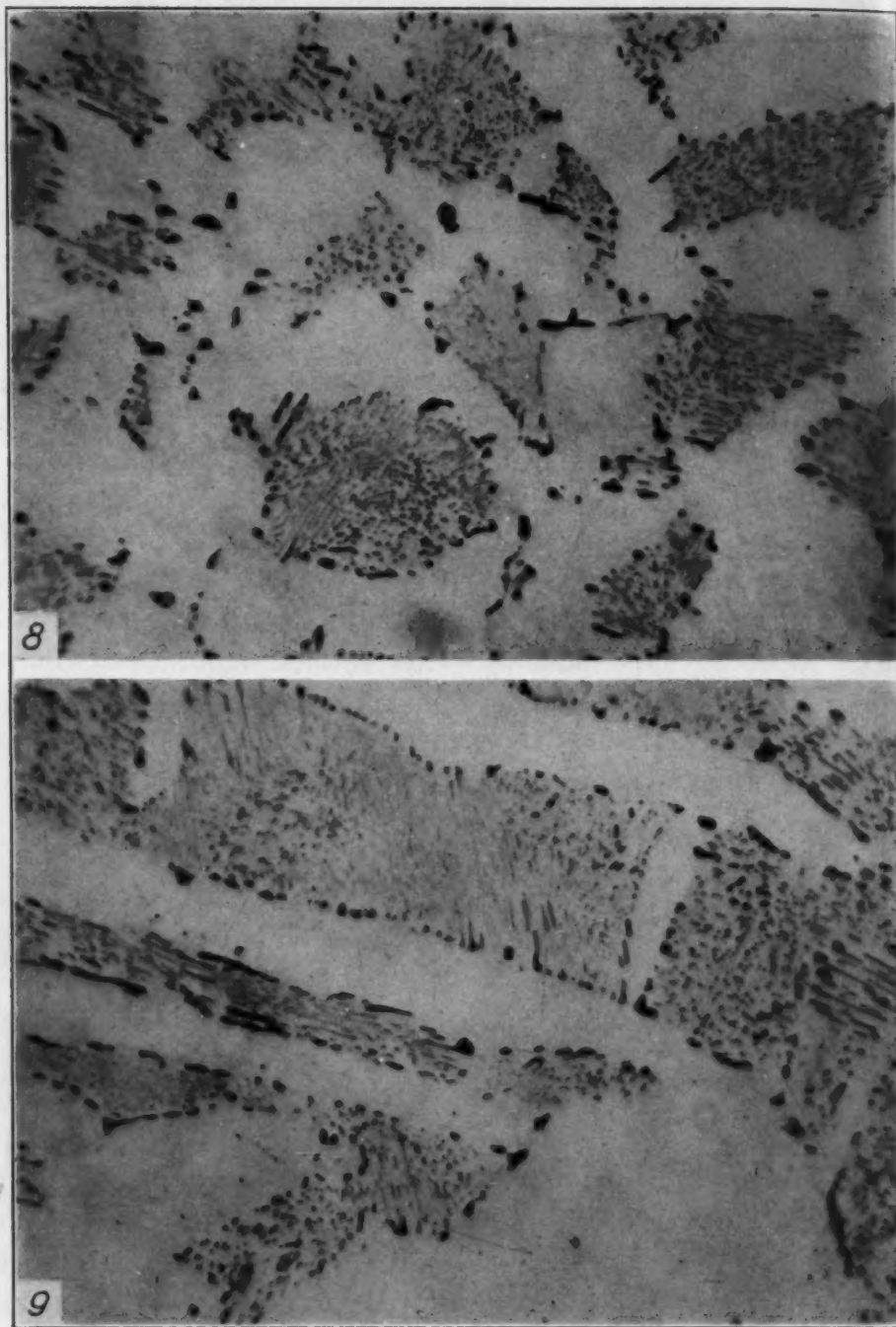


Fig. 8—Heat 3B3. Same as Fig. 5 Except at 1000 Diameters, Sodium Picrate Etch. Note Massive Carbides at Pearlite Border. (Miss Norton.)

Fig. 9—Heat 2B2. Same as Fig. 6 Except at 1000 Diameters, Sodium Picrate Etch. (Miss Norton.)

made on carburizing steels indicate that at 1500 degrees Fahr. (815 degrees Cent.) the carbon diffusion proceeds at a rate not greatly in excess of 0.001 inch per hour, but even at this slow rate of diffusion

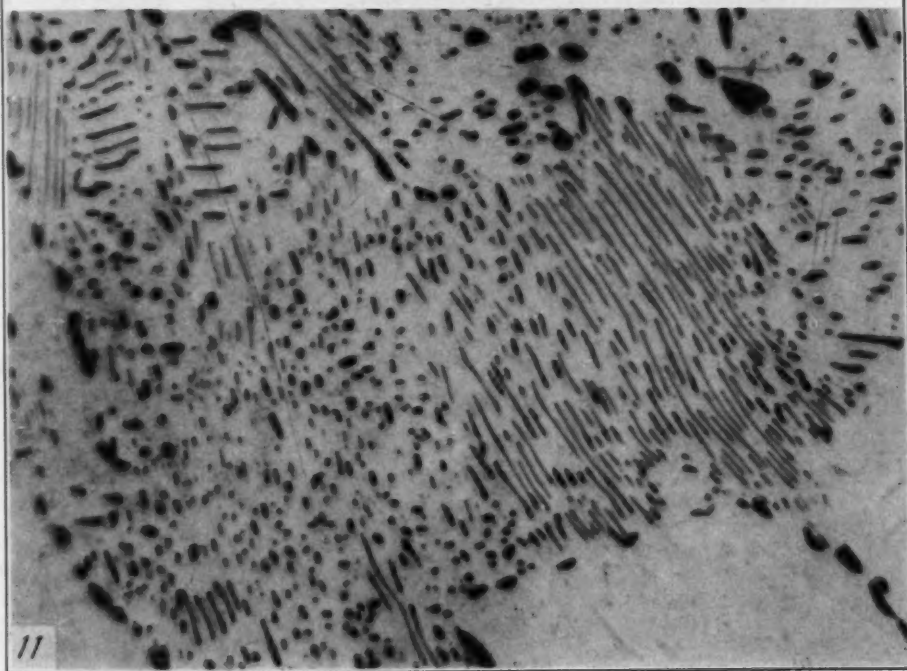


Fig. 10—Heat 5B3, Same as Fig. 7 Except at 1000 Diameters, Sodium Picrate Etch. (Miss Norton.)

Fig. 11—Heat 2B2, Structure after 24 hours at 1225 Degrees Fahr. (665 Degrees Cent.) Followed by Water Quench. At 2000 Diameters After Sodium Picrate Etch. Note the Pearlitic Structure as Compared with Figs. 8, 9 and 10. Heavy Carbide Formation is Shown Clearly at Edge of Ferrite. (Miss Norton.)

it is evident that once the carbide is in solution in the low aluminum steels the diffusion to the grain boundaries and across the grain

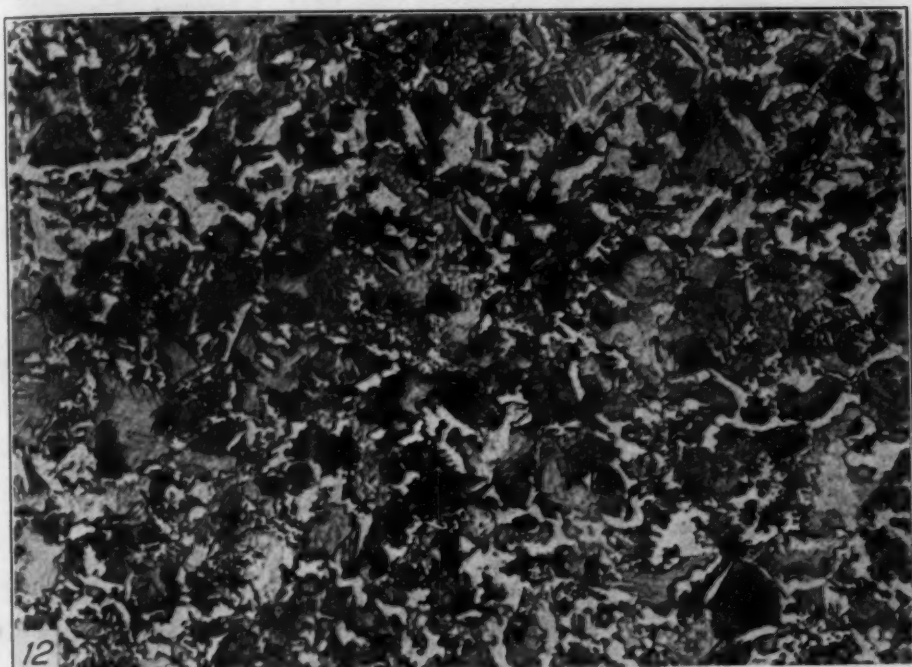
boundaries occurs in a very short time. In those steels to which aluminum has been added, such as heat 2B2 and 3B3, the distance is considerably greater and some time may be required to obtain diffusion to the grain boundaries of the carbon in solution.

The important effect of the aluminum addition seems to lie, in the heats in question, in the coarsening of the carbide which results from the thickening of the carbide plates in the pearlite. This thickening apparently starts on the exposed edges of the carbide plates close to the grain boundary where apparently the concentration of the aluminum or the effect of the aluminum compound in the ferrite is the greatest.

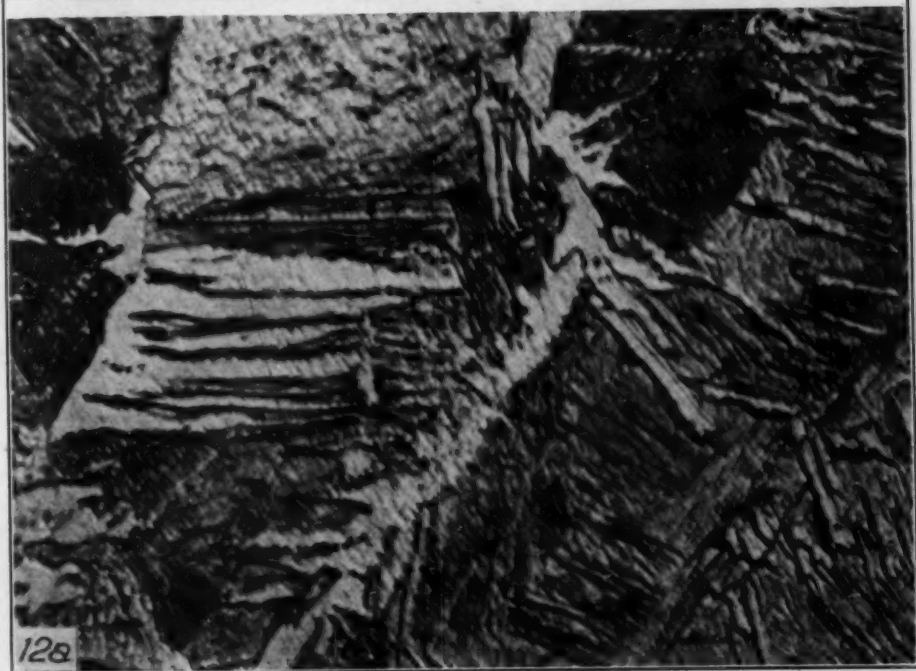
Let us examine what happens when steels having the structure indicated in Figs. 5 to 11 inclusive are heated to a higher temperature for the same time and quenched. Figs. 12 to 14 show the structures obtained at the center of 1-inch specimens which have been held for 24 hours at 1225 degrees Fahr. (665 degrees Cent.) and then transferred to a furnace at 1500 degrees Fahr. (815 degrees Cent.) and held for 15 minutes and then quenched in cold water. It is evident that none of these heats showed complete solution, heat 3B3 being the least affected and heat 5B3 being the most affected by the quench. There is considerable evidence of martensite, especially in the center of the grains in these heats, but there is still considerable excess ferrite evident.

Fig. 15 shows the Rockwell hardness test across the face of the 1-inch bar indicating the greater hardenability of the lower aluminum steel, but also showing that complete hardenability had not been obtained in any of the heats except near the surface of the bars. Fig. 16 shows the structure obtained in heat 2B2 after the treatment indicated, showing the relative amounts of martensite, sorbite, ferrite, etc. at 1000 diameters.

Figs. 12A, 13A and 14A show the structures obtained on heating samples from heats 3B3, 2B2, and 5B3 to 1500 degrees Fahr. in lead and holding at temperature for 15 minutes and water quenching. The samples so treated were not held at temperatures below the critical range for more than the very minimum of time but were in the normalized condition previous to heat treatment. Figs. 12A, 13A and 14A should be compared to Figs. 12, 13 and 14. The effect of the long hold at a temperature below the critical range is indicated clearly by comparing Figs. 14 and 14A. When the normalized steel containing low aluminum addition (Heat 5B3) was heated rapidly



12



12a

Fig. 12—Heat 3B3. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to 1500 Degrees Fahr. (815 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. Note the Small Grain Size, the Free Ferrite and the Presence of Martensite in Some of the Grains. (Miss Norton)

Fig. 12A—Heat 3B3. Structure Obtained After Heating in Lead to 1500 Degrees Fahr. (815 Degrees Cent.) and Holding for 15 Minutes at this Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 1500 Diameters, Nital Etch. Note the Amount of Free Ferrite, and Compare with Figs. 12 and 20. (Guthrie and Lottier)

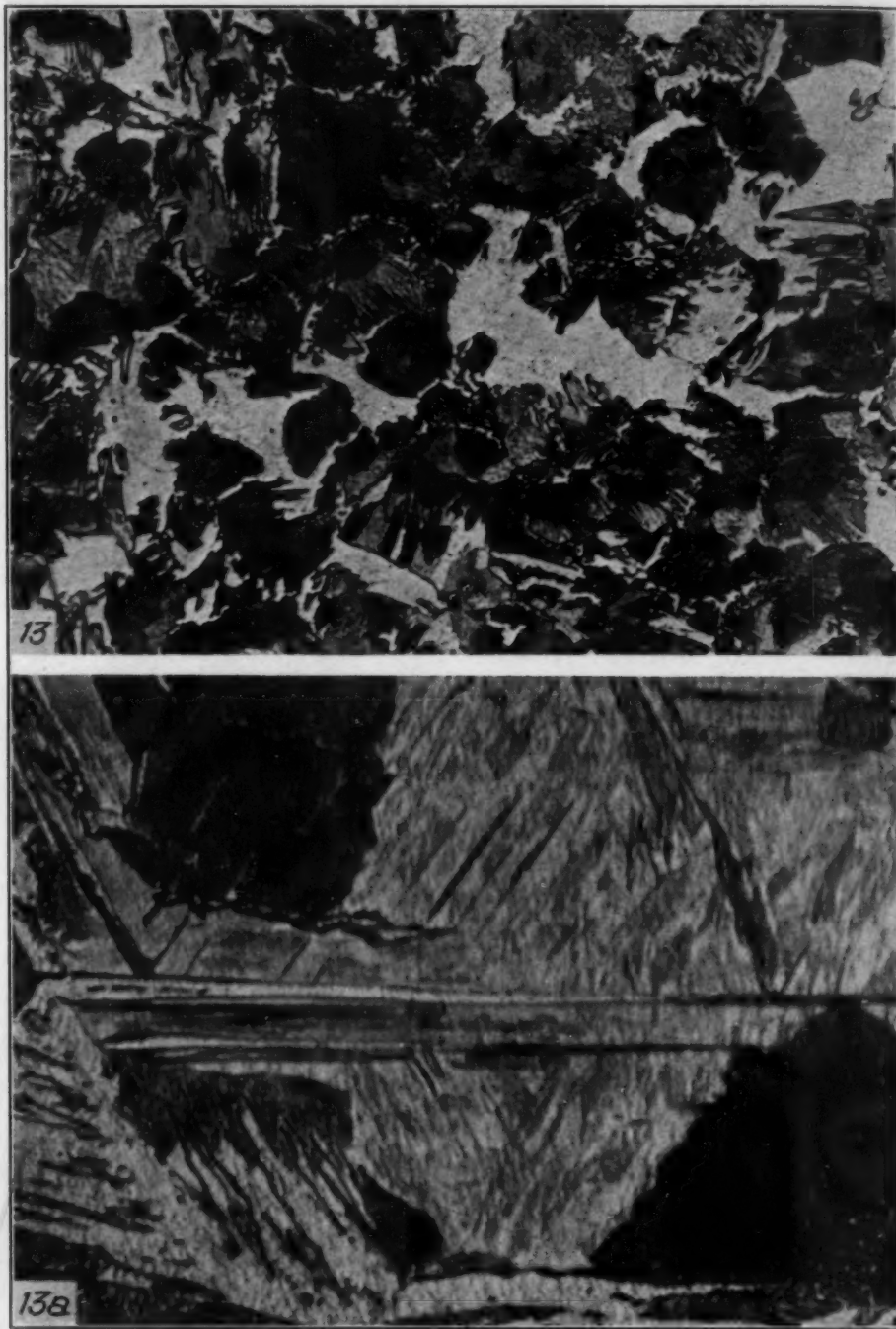


Fig. 13—Heat 2B2. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to 1500 Degrees Fahr. (815 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. Note Free Ferrite. (Miss Norton)

Fig. 13A—Heat 2B2. Structure Obtained After Heating in Lead and Holding at 1500 Degrees Fahr. (815 Degrees Cent.) for 15 Minutes, Following by Water Quench. Structure Obtained at Center of 1-inch Specimen. 1500 Diameters, Nital Etch. Compare with Figs. 13 and 22. (Guthrie and Lottier)

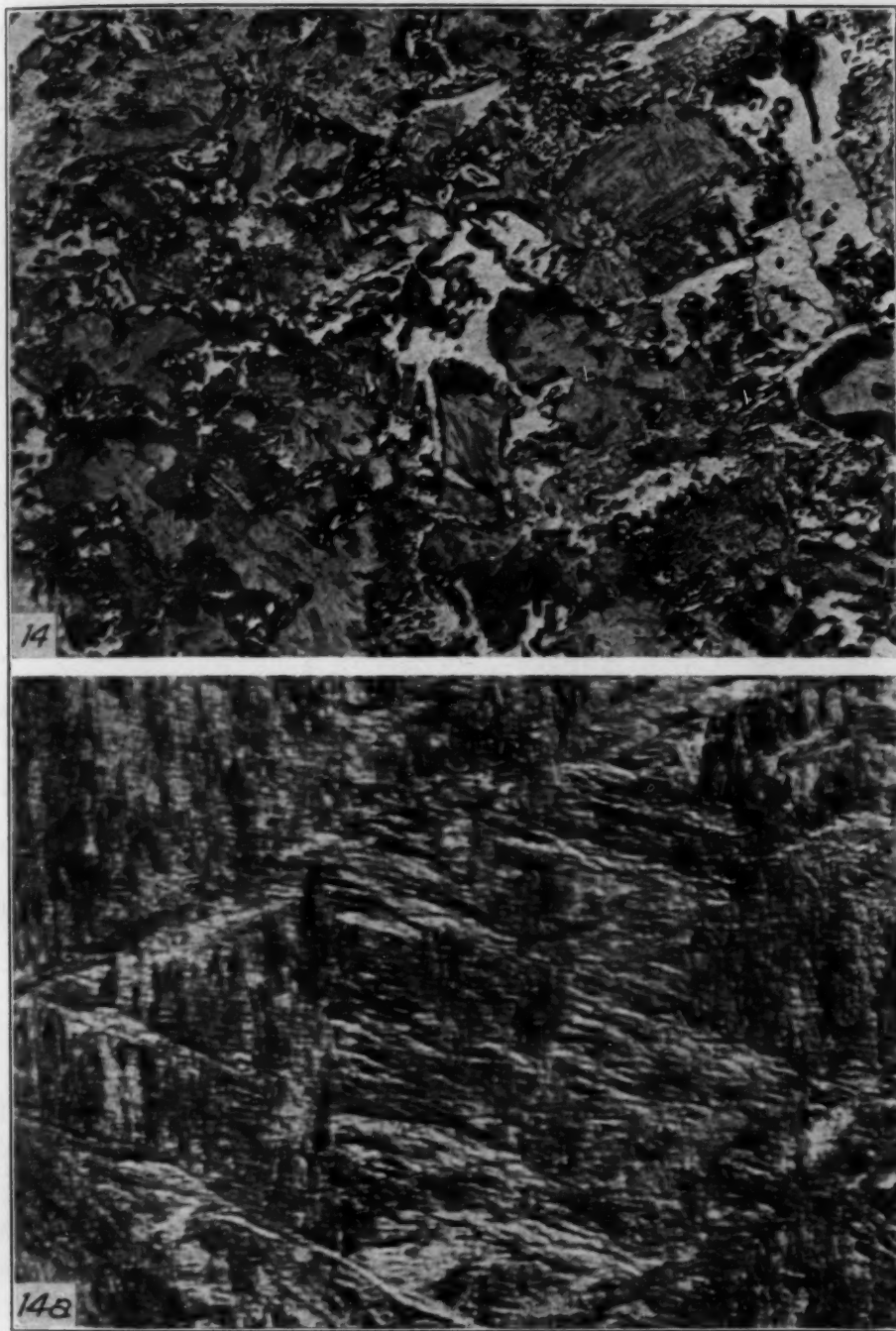


Fig. 14—Heat 5B3. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to 1500 Degrees Fahr. (815 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. (Miss Norton)

Fig. 14A—Heat 5B3. Structure Obtained After Heating in Lead to 1500 Degrees Fahr. (815 Degrees Cent.) and Holding for 15 Minutes at this Temperature, Following by a Water Quench. Structure Obtained at the Center of 1-inch Specimen. 1500 Diameters and Nital Etch. Compare with Figs. 14 and 23. (Guthrie and Lottier)

in the lead bath from the normalized condition, the carbides were completely in solution, after 15 minutes at 1500 degrees Fahr.

Since the usual time in commercial practice for heating 1-inch bars of this analysis for quenching would be usually not over ten

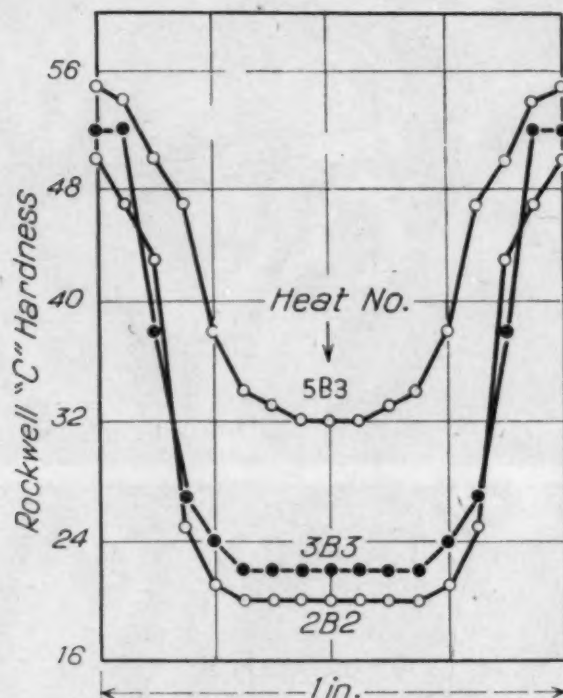


Fig. 15—Curve Showing Rockwell Hardness Readings on 1-inch Test Specimens after Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to Furnace at 1500 Degrees Fahr. (815 Degrees Cent.) for 15 Minutes and Water Quenching.

minutes at a temperature of 1500 degrees Fahr. (815 degrees Cent.) it is quite evident that the holding at 1225 degrees Fahr. (665 degrees Cent.) for 24 hours had resulted in an important decrease in the rate of solution of the carbide in the austenite as compared to a steel treated in the usual manner. This serves to indicate the magnifying action of the coalescing treatment on the hardenability of the steels. It is interesting to note that the apparent difference in grain size between heat 3B3 after this treatment and 2B2 had not resulted in any particular difference in hardenability, which seems to be in this case influenced by other factors than the grain size.

Figs. 17 to 26 inclusive show the structures obtained by holding specimens of the three heats being investigated at a temperature of 1225 degrees Fahr. (665 degrees Cent.) for 24 hours, transferring

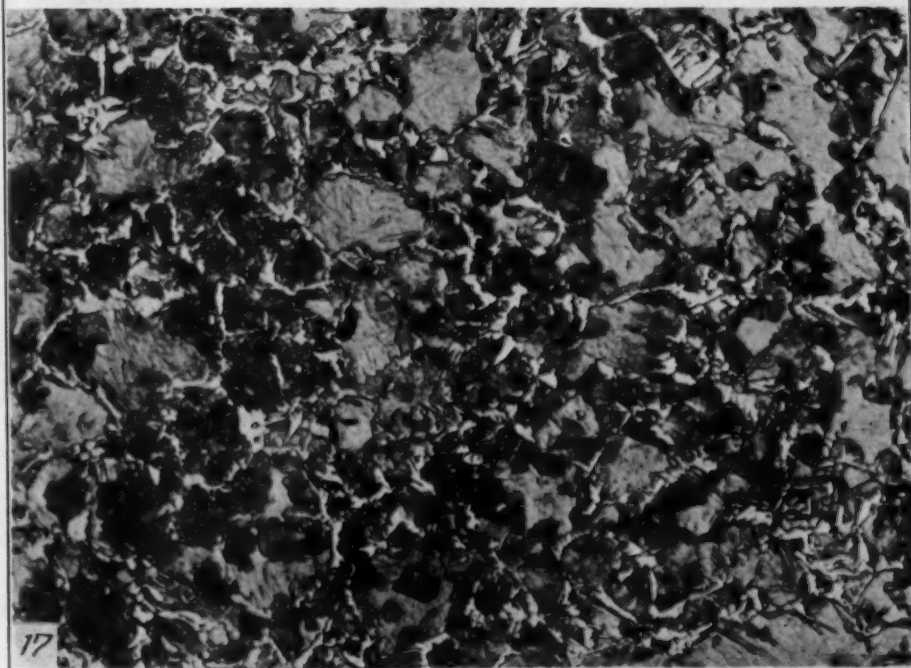
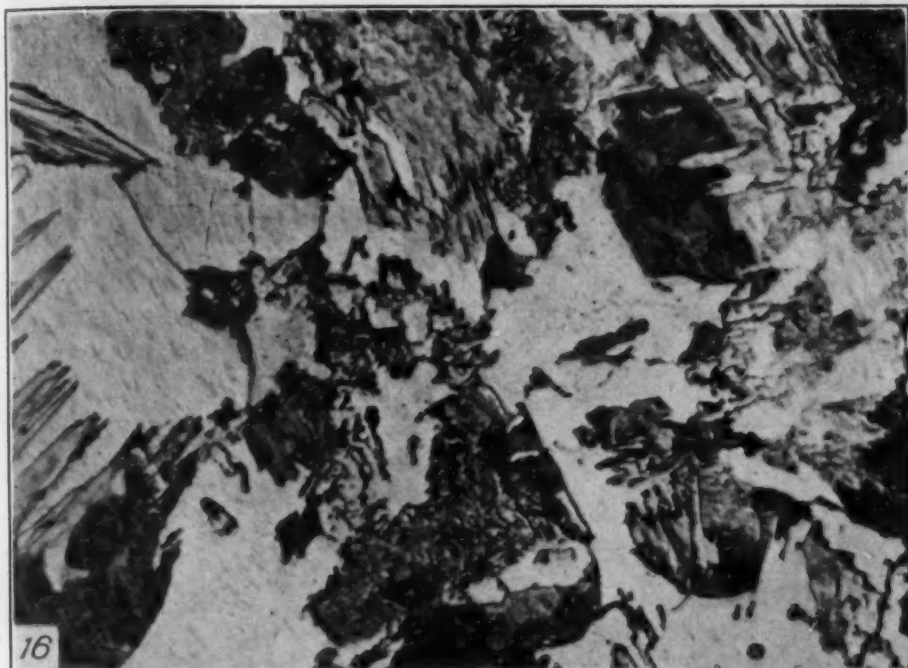


Fig. 16—Heat 2B2. Same as Fig. 13 but at 1000 Diameters. Note Ferrite, Martensite and Sorbitic Structures. (Miss Norton)

Fig. 17—Heat 3B3. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, transferring to 1700 Degrees Fahr. (930 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Followed by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. Note Grain Size and Compare with Fig. 12. (Miss Norton)

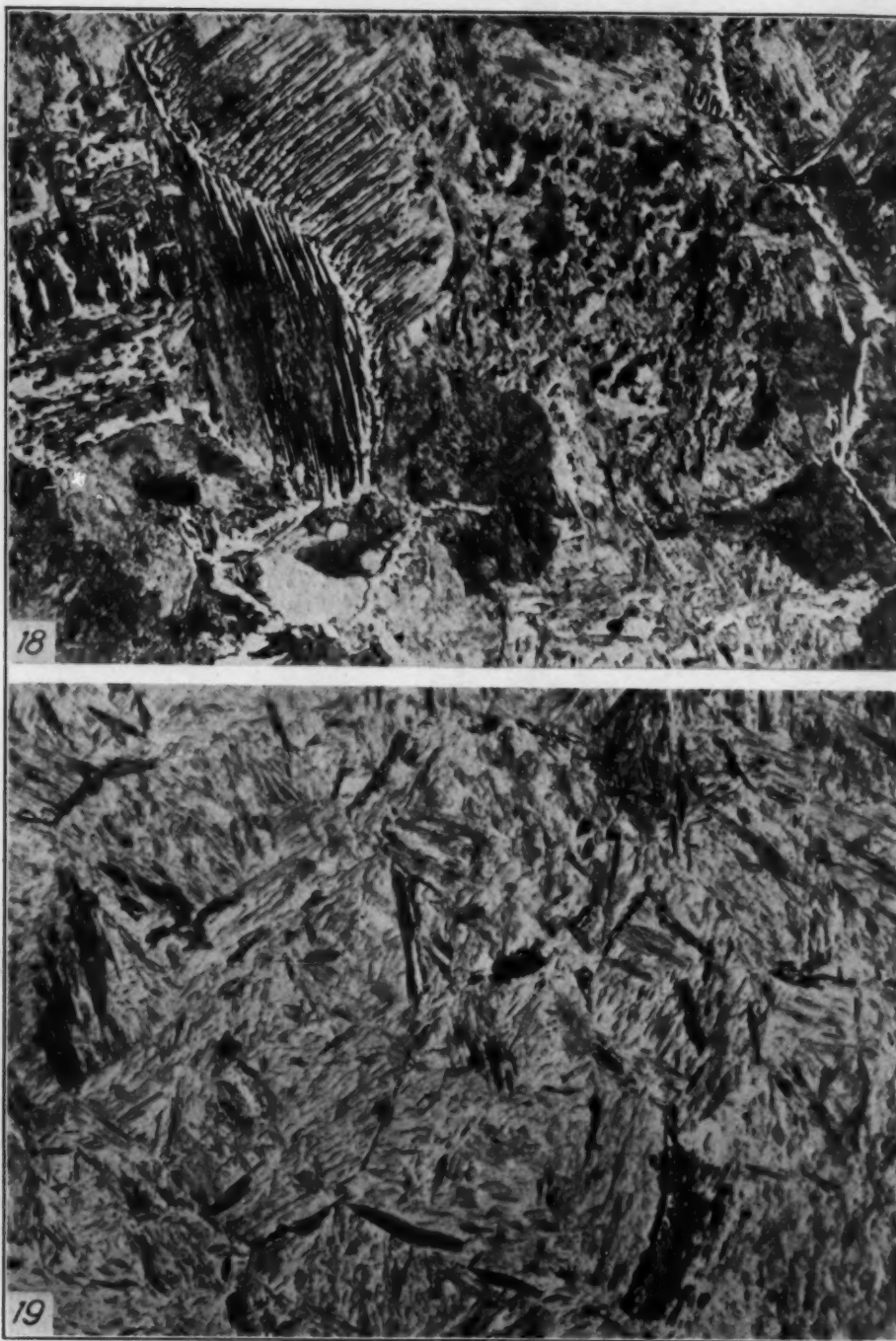


Fig. 18—Heat 2B2. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to 1700 Degrees Fahr. (930 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. Note Martensite at Center of Grain with Free Ferrite in Grain Boundary. Note Elimination of Grain Boundary and Complete Solution and Diffusion of Carbon. (Miss Norton)

Fig. 19—Heat 5B3. Structure Obtained After Holding at 1225 Degrees Fahr. (665 Degrees Cent.) for 24 Hours, Transferring to 1700 Degrees Fahr. (930 Degrees Cent.) Furnace and Holding for 15 Minutes at Temperature, Following by a Water Quench. Structure Obtained at Center of 1-inch Specimen. 450 Diameters, Nital Etch. Note Absence of Ferrite and Almost Complete Martensite Structure. (Miss Norton)

them to a furnace at 1700 degrees Fahr. (930 degrees Cent.), holding them at this temperature for 15 minutes and quenching in water.

A study of Figs. 17, 18 and 19 will develop that heat 3B3 shows practically no grain growth and still has a definite ferrite envelope surrounding each grain which consists in some cases of a fine sorbitic structure and in others of a martensitic structure surrounded by a sorbitic envelope, indicating incomplete solution and diffusion of the carbon in these grains. Figs. 18 which shows the structure at the center of a 1-inch specimen from heat 2B2 shows a much larger grain size than is the case with heat 3B3, Fig. 17. The martensitic centers in the grain, with the lower carbon sorbitic zone adjacent to the grain boundary, is typical of this heat after the treatment given. There is still considerable ferrite in evidence around the grain boundaries although in some cases the diffusion of carbon has eliminated the grain boundary and resulted in grain growth. Fig. 19 shows the structure obtained from heat 5B3 treated as above, and shows almost complete solution of carbide as well as complete diffusion of the carbon, so that the only remaining evidence of grain boundary is found in occasional boundary ferrite or troostite. Figs. 20, 22 and 23 show the structure obtained at 1000 diameters from the same specimens as Figs. 17, 18 and 19. The increased magnification shows more clearly the characteristic structures, indicating the large amount of ferrite which was typical of heat 3B3 and the almost complete martensitic structure typical of heat 5B3. From Fig. 22 it is evident that the martensitic areas correspond to the original pearlitic zones shown in Figs. 3, 6 and 9, indicating that apparently the lamellar pearlite goes very quickly into solution, but that the coalesced carbides at the edge of the carbide plates have resisted solution so that the boundary areas corresponding to the free ferrite in Fig. 22 are apparently lower in carbon and hence did not form martensite at the speed of quenching used. The presence of the ferrite envelopes indicates that either diffusion of the carbon had not been sufficient to completely obliterate the grain boundary ferrite or that the solubility of the carbon in the grain boundary ferrite itself had been greatly decreased as compared to the remainder of the grain. It is interesting to note that where the carbon had diffused to the grain boundaries that the final result had been a complete elimination of the grain boundary ferrite and the resulting merging of two grains of austenite into one. This offers a possible explanation for grain growth as well as grain-size phenomena, by indicating that the

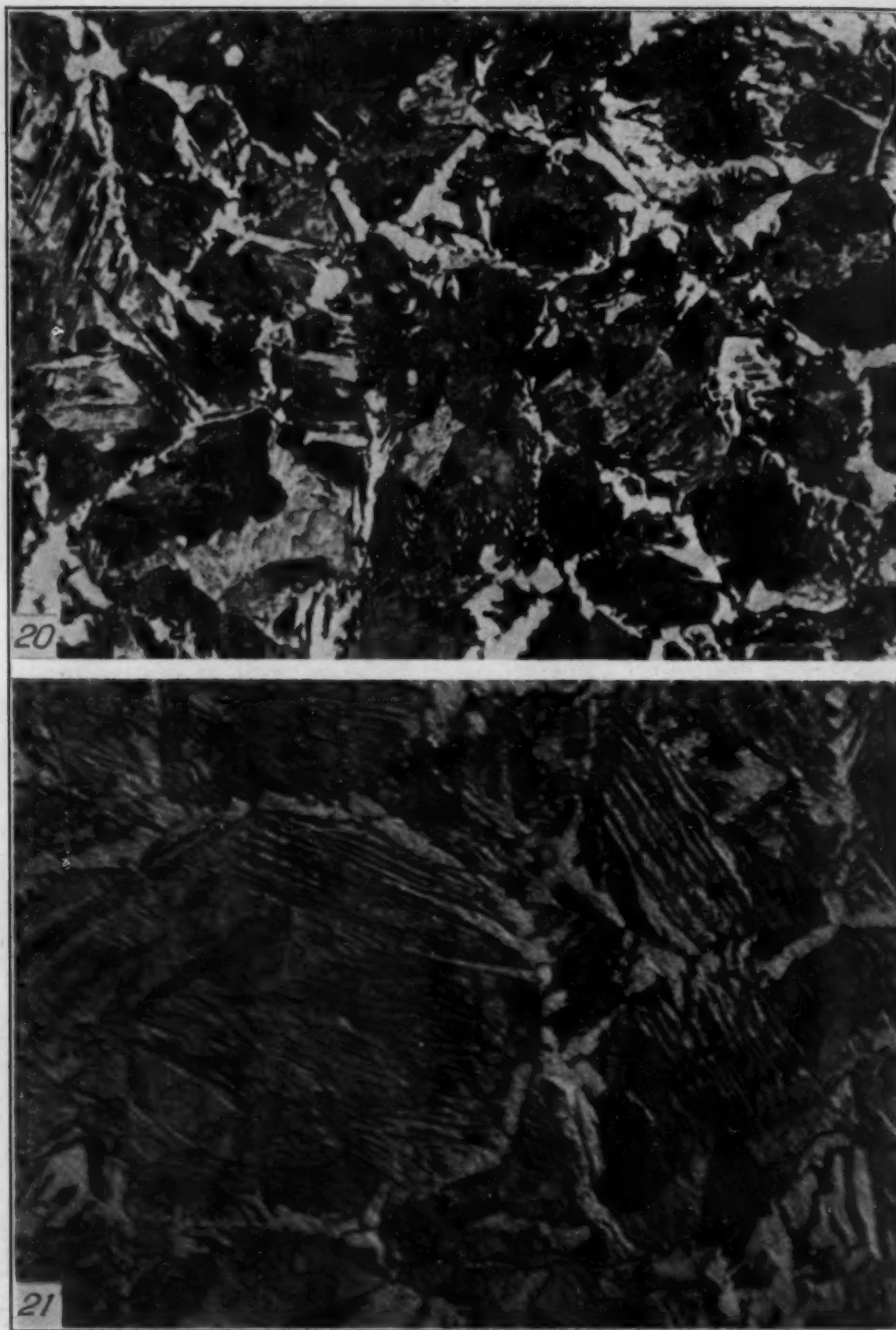


Fig. 20—Heat 3B3. Same as Fig. 17 but at 1000 Diameters. (Miss Norton)

Fig. 21—Heat 3B3. Same as Fig. 17 but at 1500 Diameters. Structure Shown Near Surface of Quenched 1-inch Bar, Indicating the Excessive Amount of Free Ferrite still Evident even after Very Rapid Cooling from 1700 Degrees Fahr. (930 Degrees Cent.). (Guthrie and Lottier)

explanation for grain growth might be in the obliteration of the final free austenite envelopes by the diffusion of carbon. Thus it might be speculated that when carbon diffusing towards the grain

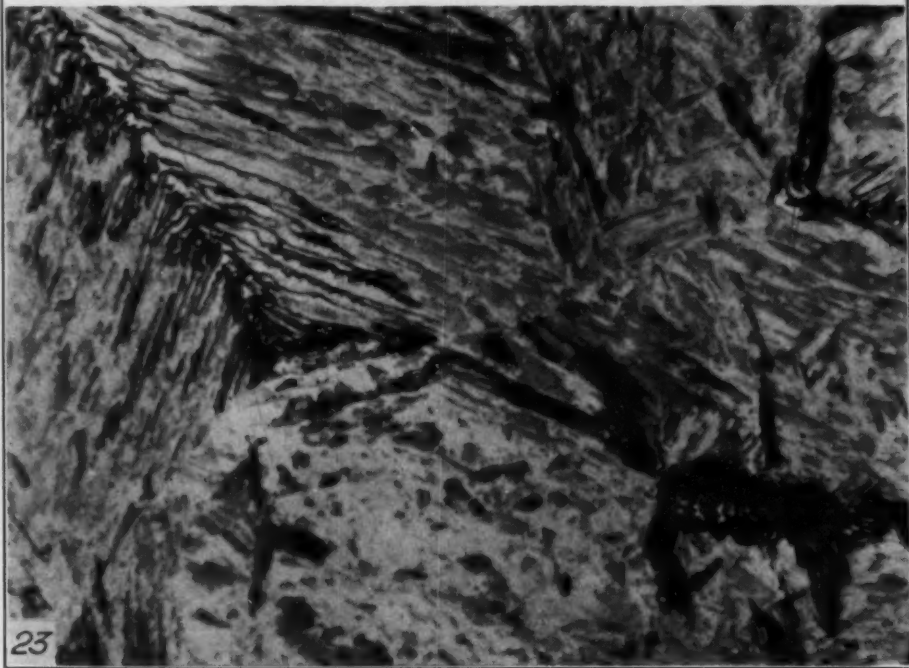
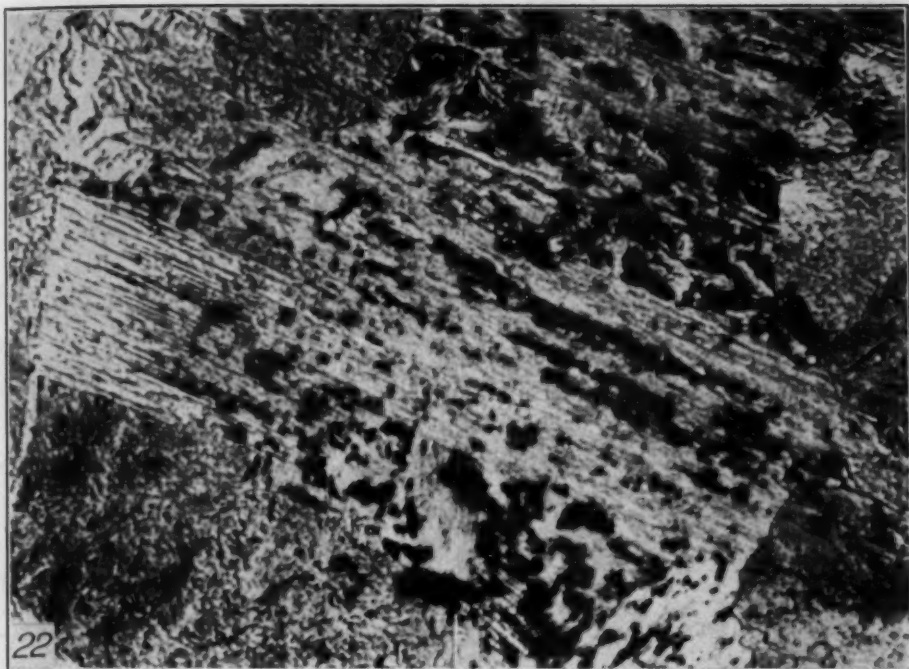


Fig. 22—Heat 2B2. Same as Fig. 18 but at 1000 Diameters. Note Edge of Martensitic Sorbitic Structure and Compare with Figs. 3, 6 and 9. (Miss Norton)

Fig. 23—Heat 5B3. Same as Fig. 19 but at 1000 Diameters. Note Free Ferrite in Grain Boundary. (Miss Norton)

boundary from the carbide in solution progresses to the point where the last traces of free austenite are eliminated that there is a tendency for the grain boundary to be eliminated by the combining

of one austenitic grain with the others. This would explain the effect of the carbide on grain growth and grain size and would also explain why the austenite grain in the higher carbon steels might grow more rapidly on heating than would the lower carbon austenitic grain. It will explain the inhibiting action of the excess carbide in the hypereutectoid zone of carburized steel when these carbides are relatively massive, and their possible accelerating action on grain growth when they are fine. Fig. 21 shows the practically unchanged grain size of heat 3B3, although the presence of a considerable amount of martensite is evident. There is still sufficient excess ferrite in the grain boundaries to indicate that carbon solution and diffusion had not proceeded sufficiently fast to obtain a satisfactory over all hardness. Figs. 24 to 27 inclusive show sodium picrate etches of the three heats after the treatment given and indicate clearly the presence of the three structures, i. e., martensite, ferrite and sorbite. Fig. 28 shows the hardness across the 1-inch bar as measured by the Rockwell test. It indicates very clearly the practically complete hardening of the low aluminum steel and the relatively low hardenability of the higher aluminum steels.

The term "hardenability" in reference to any element in steel should be carefully used since what is usually meant by this term is the effect of the certain element on the measured hardness after heating to a given temperature and for a given time in conjunction with a certain rate of cooling. E. Houdremont, H. Bennek, and H. Schrader, in a paper presented to the A. I. M. E. last year, indicated clearly the effect of carbide solution on the results obtained in quenching. They indicated that at the proper temperature and with the proper time, none of the commonly added elements which form carbide such as tungsten, molybdenum, chromium, vanadium, etc., could be properly termed shallow hardening. In fact, when these carbides were finally dissolved in the austenite the results indicate that they produce deep hardening even with aluminum. The aluminum-bearing steels, it is believed, are shallow hardening only when the time and temperature are insufficient to obtain complete carbide solubility and carbon diffusion through the grain boundaries. If the time and temperature are insufficient to obtain this condition, we have essentially a lower carbon steel, especially at the grain boundaries. It is necessary, when elements are added which decrease the solubility of the carbides, that the temperature must be increased considerably to obtain complete solution as evidenced by the tempera-

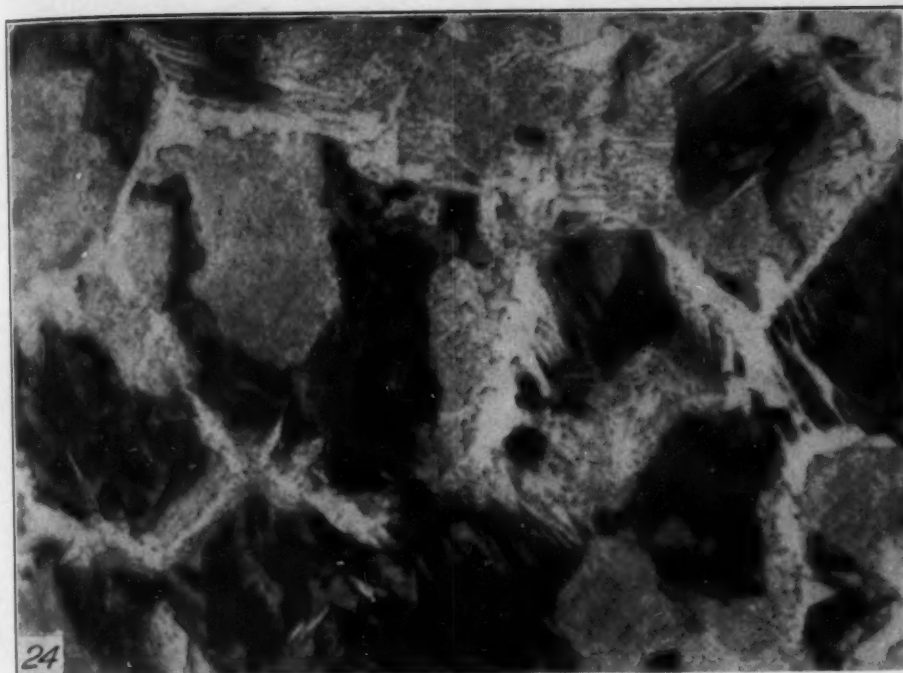


Fig. 24—Heat 3B3. Same as Fig. 20 Except Sodium Picrate Etch at 2000 Diameters. (Miss Norton)

Fig. 25—Heat 2B2. Same as Fig. 22 but Sodium Picrate Etch at 2000 Diameters.

tures required to satisfactorily fully harden such steels as our nitriding steel and high speed steels.

It is interesting to note that heat 2B2, in spite of the large increase in grain size, shows very little increased hardenability as com-

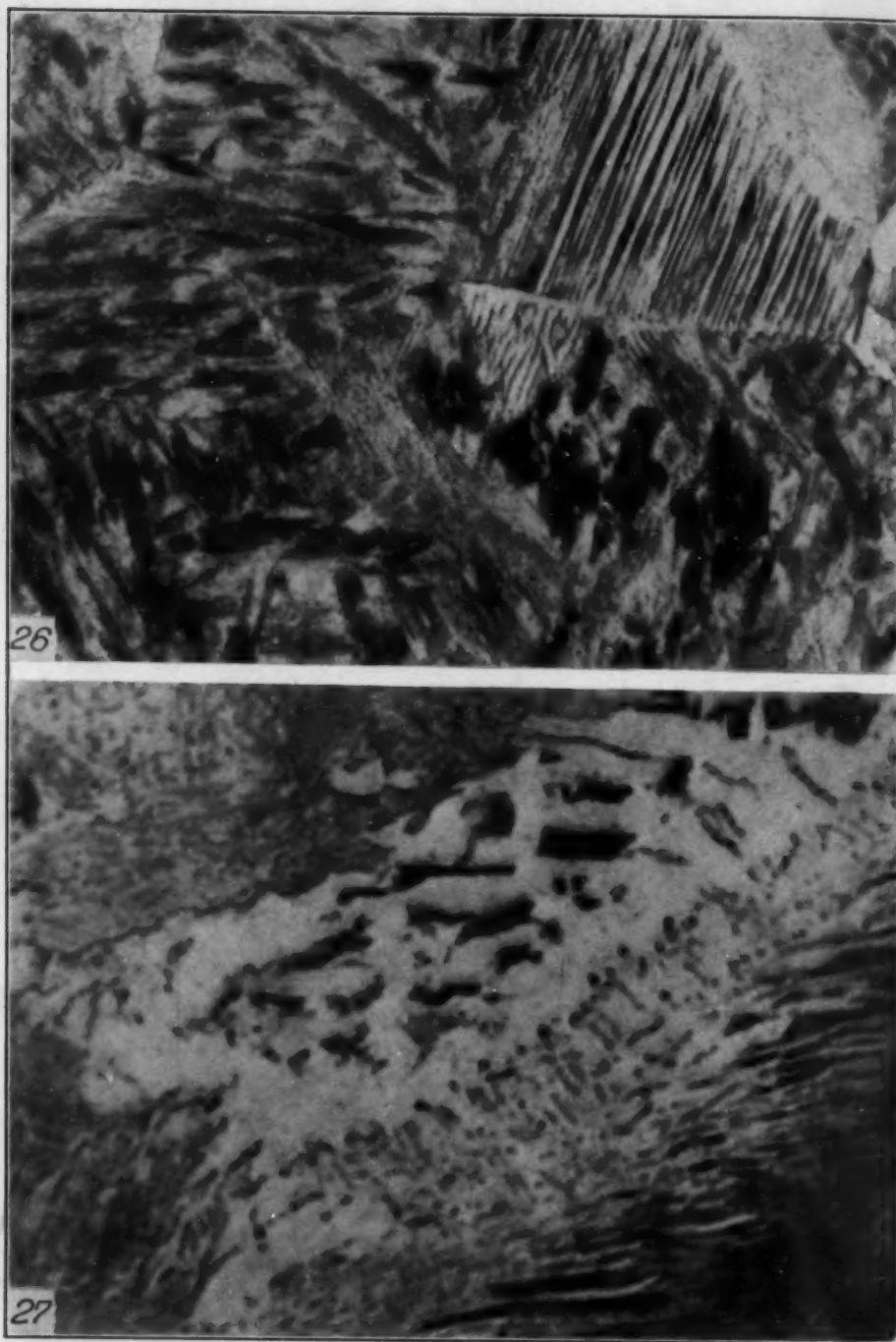


Fig. 26—Heat 5B3. Same as Fig. 23 but at 2000 Diameters in Sodium Picrate Etch. Note Apparent Method of Carbide Solution and Diffusion where Free Ferrite is still Evident. (Miss Norton)

Fig. 27—Heat 2B2. Same as Fig. 25 but at 3500 Diameters in Sodium Picrate Etch. (Miss Norton)

pared to heat 3B3, due primarily to the fact that a considerable portion of the carbide is not yet in solution.

Inasmuch as the primary variation in these heats is in the alumi-

num addition, it would seem that the important effect of the aluminum is to vary the hardenability, not by grain size variation but rather by structural variation since in spite of the difference in grain size between heat 3B3 and 2B2, as shown by Figs. 17 and 18, the hardenability is not markedly different. By grain size is meant in this case the structural grain size as shown by the photomicrographs

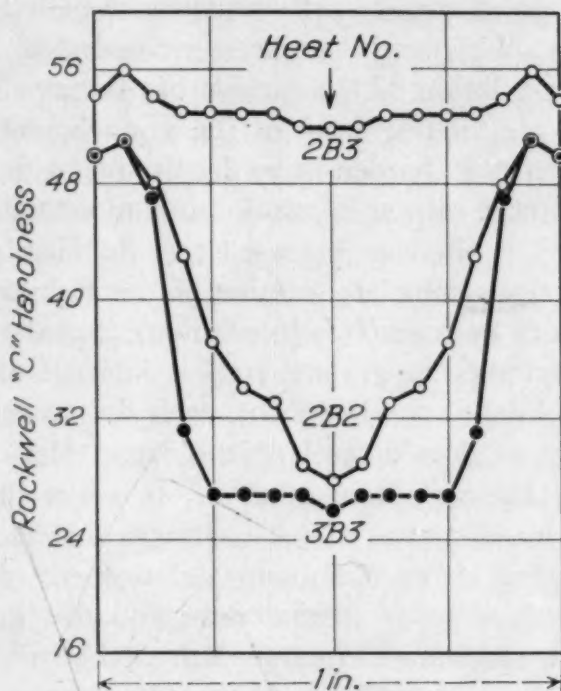


Fig. 28—Curve Showing Rockwell Hardness Readings on 1-inch Test Specimens After Holding for 24 Hours at 1225 Degrees Fahr. (665 Degrees Cent.), Transferring to Furnace at 1700 Degrees Fahr. (930 Degrees Cent.) for 15 Minutes and Water Quenching.

after heating to 1700 degrees Fahr. (930 degrees Cent.) for 15 minutes, and not by the structure developed by the McQuaid-Ehn test.

Since there would be less carbon in the ferrite in the grain boundary of heats 2B2 and 3B3 when heated at the usual temperature and for the usual time, the precipitation of ferrite in the grain boundaries would be more easily obtained unless the cooling rate was greatly increased so that we have the effect of a lower carbon steel when the carbides are not completely in solution and this lower carbon region is confined primarily to the grain boundaries. For this reason, for the same particular type of quenching, there is a greater tendency to form ferrite boundaries in the steels having carbides out of solution.

It must be remembered that this is only true in those steels

which are reheated in a pearlitic condition and would not necessarily be true of steels which had been previously quenched or completely spheroidized before reheating.

It would seem then that grain growth and grain size are perhaps resultant effects of carbide solubility and hence are only a secondary indication of the ability of a piece to harden and, therefore, the assumption that grain size is in itself the cause of hardenability may not be true. In other words, a coarse-grained steel may be coarse because complete solution of the carbide has occurred, and diffusion has taken place, obliterating most of the grain boundaries. Thus a coarse-grained steel will harden more deeply than a fine-grained steel because we have more carbon in solution in a more stable condition so that hardenability is thereby increased and ductility decreased. In the fine-grained steels complete solution of the carbide has not taken place and therefore less carbon is in solution particularly at the grain boundaries so that the fine-grained steel is in itself an indication of partial carbide solubility and hence the steels do not possess the same hardening ability as does a steel of the same total carbon content but which has all the carbide in solution. It is a well known fact to those who have made studies of grain growth that the so-called silicon-killed steels free from aluminum and properly deoxidized, exhibit grain growth at a low temperature and this grain growth is completed in a narrow range of temperature. This is what would be expected in this type of steel where the free ferrite is a minimum and where the maximum amount of pearlite is present. On the other hand, it is also well known that in the so-called aluminum-killed steels of fine grain type, or those steels which are less completely deoxidized, do not exhibit this sudden tendency to complete grain growth over a narrow temperature range but exhibit rather a tendency towards a gradual grain growth over a considerable temperature range. This is as would be expected if we are to consider that grain growth is effected only by the diffusion of carbon through the grain boundaries after solution of the carbides. In the aluminum-treated steels there is, of course, a very great variation in the carbide particle size depending upon the time-temperature combination which permits coalescence at temperatures just under the critical range.

It is interesting to note that iron oxide (FeO) acts in a similar manner to aluminum and vanadium, probably by remaining in solution in the ferrite, particularly in the grain boundary, causing a differential solubility of carbide which reaches a maximum at the cen-

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ter of the grain and a minimum in the grain boundary. This is important in that both aluminum and FeO affect the austenite transformation rate both on heating and cooling and the rate at which the austenite transforms and the shape of the transformation curve is affected by both aluminum and iron oxide.

It is a well known fact that one of the effects of undercooling is to reduce the size of precipitated particles so that one of the important effects of drastically undercooling a solution is to obtain a precipitate which is in the finest possible condition. This is what happens, of course, when a steel in the austenitic condition, containing carbides in solution, is drastically undercooled by severe quenching. In this case the carbides are precipitated in the finest possible form uniformly distributed throughout, resulting in the hardest and strongest structure. One of the effects of aluminum and iron oxide in solution is apparently the reduction of the undercooling which can be obtained with a given speed of quenching. This results in a precipitation of carbides at a much higher temperature and hence the precipitation of much larger carbides, with resultant decrease in hardness. The total volume of the carbide in a steel containing a given percentage of carbide in solution should be the same on precipitation whether the transformation takes place at a high or low temperature. With drastic undercooling, this carbide precipitates in a very fine form in a rigid ferrite, so that the work hardening which would occur due to this fact would be great. When the carbide precipitates out in a more ductile ferrite and in a larger unit mass, which would occur at higher transformation temperatures, the hardening due to the carbide precipitation would be relatively small.

In the paper presented by Mr. Ehn and the writer² in 1922, the effect of the oxide in solution on the carbide form was quite clearly indicated, although the connection between the carbide form and the results obtained in heat treatment were not clearly connected. It is believed that concentration of the oxide is higher in the grain boundaries with the result that steels high in FeO resist carbide solution in the grain boundary so that it is difficult to quench steel of this type without obtaining some free ferrite in the grain boundaries. This free ferrite is, of course, an important factor in increasing the ductility but a detrimental factor if maximum hardness is required. It is quite possible that the aluminum effect is also somewhat greater

²H. W. McQuaid and E. W. Ehn, "Effect of Quality of Steel on Case Carburizing Results," *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 67, p. 341, 1922.

in the grain boundary than at other portions in the grain, due to the fact that the amount of other residual compounds and elements are a maximum in the grain boundary so that the combined effect is to increase the temperature at which the carbide is precipitated and hence the tendency for the carbide to reach a maximum particle size.

A similar effect on the carbide size would be found in highly segregated areas of oxide or aluminum such as would be found in a ghost line. One of the characteristics of ghost lines on the structure is the rejection of carbide from the saturated areas and, as a carburizing test will show, a tendency to produce carbide in a more massive form.

It might be possible that when FeO is the cause of the so-called abnormality in steel that this effect can be reduced or entirely removed by carburizing in a hydrocarbon gas which reacts with the FeO and possibly actually eliminates it. This effect of the hydrocarbon would be very greatly reduced, if not entirely absent, where aluminum is the cause of the "abnormal" carbide formation. This would explain the variation in results which have been obtained by different investigators when using a hydrocarbon gas for making the standard carburizing test.

If, as we believe, we are primarily more interested in the carbide characteristics of a given steel than we are in grain size, it is the author's opinion that the use of the carburizing test as a means of indicating the relative hardenability characteristics in a given heat of steel should still be satisfactory. The temperature usually used (1700 degrees Fahr.) represents approximately the maximum which would usually be reached in commercial heat treatment. The rate of heating and the rate of cooling is slow enough to develop the tendency of the carbides to thicken up at subcritical temperatures, and the use of the hypereutectoid carbide as an indication of this same tendency should be especially satisfactory. However, one of the difficulties has been that we are often interested in steels which in their carbide thickening characteristics lie between the extreme cases of fine lamellar pearlite and the extremely abnormal type of high aluminum or overoxidized steel. Since this is the case, the grain size, as developed by the carburizing test or by a high temperature heat treatment is a fairly sensitive indication of the ability of the carbides to go into solution and the carbon to diffuse across the grain boundary so that an examination of grain size alone is of considerable value and probably satisfactory for most commercial uses.

The above conception of carbide solubility and variable carbon diffusion as one of the causes of variation in hardenability and related physical properties has been found to be of considerable value in explaining some of the effects of low temperature heat treatment, i. e., heat treatment below the critical range. The effect of long time drawing at temperatures below the critical range has been well known for many years to those who have had to obtain maximum ductility for a given tensile strength specification. As a preparatory treatment to hardening to improve ductility, decrease warpage, and improve resistance to shock loading, the application of the above thoughts has been found to be of practical value.

The writer is fully aware that many of the opinions expressed in this paper do not conform to commonly accepted explanations for some of the results obtained. They are offered primarily to stimulate a greater concentration of thought on carbide solution and carbon diffusion rates and the general effect of carbide particle size on the properties of heat treated steels.

DISCUSSION

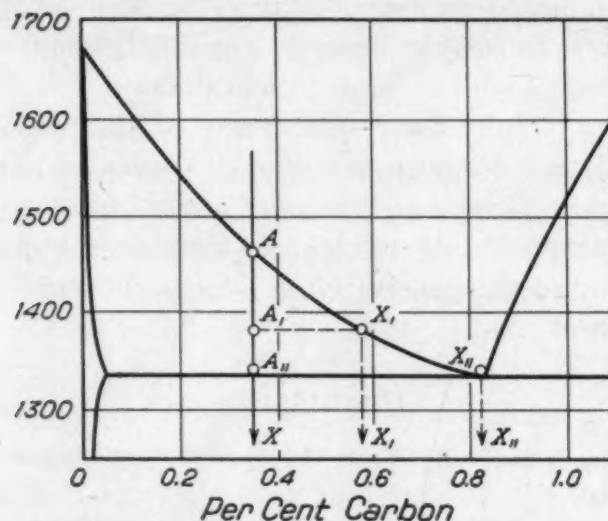
Written Discussion: By F. B. Foley, research department, Midvale Co., Philadelphia.

The idea propounded by Mr. McQuaid that it is aluminum in solution in steel, and not the presence of alumina particles, which is effective in modifying the austenitic grain size, has more in its favor than any of the hypotheses so far advanced. His conclusions are strengthened by further analysis of the effects on ferrite of the presence of aluminum in solution. Undoubtedly, aluminum decreases the solubility of carbon in ferrite and also in austenite and it is because of this that it is able to restrain the growth of austenite grains. McQuaid contends that it is the ease with which carbides agglomerate in aluminum-bearing ferrite, and the consequent slowness with which these more massive carbides pass into solution in austenite, that is in a larger measure responsible for the effect of aluminum in controlling grain size.

Aluminum, like silicon, nickel and those elements which are soluble in ferrite and do not form carbides, promotes the formation of graphite, decreases the solubility of carbon in steel and retards diffusion of carbon. Aluminum also raises the A_1 point of steel very rapidly. With as little as 1.2 per cent of aluminum present the A_3 point of iron is raised and the A_1 point lowered, forming a closed gamma loop.

With these ideas in mind it is possible to explain, by tracing the mode of transformation, how aluminum affects the grain growth of austenite. In the conventional sketch of the carbon-iron diagram in accompanying figure, assume an aluminum-free hypoeutectoid steel of carbon represented by the vertical line "x" to be heated to the point A_{11} . At this temperature the eutectoid (X_{11}) transforms to austenite, the structure then consisting of austenite crystals

of eutectoid carbon surrounded by a ferrite envelope. Upon further heating to A_1 some of the ferrite into which carbon from the austenite has diffused transforms to austenite, the structure at this point consisting of austenite crystals of carbon X_1 surrounded by a ferrite envelope. Finally at A , carbon from the austenite has diffused into the ferrite envelope so that practically all the ferrite has attained a carbon content X and the structure of the alloy is entirely face-centered austenite of carbon X . This method of viewing the progress of transformation of a Fe_3C plus Fe structure to a pure austenite is based on the gradual diffusion of carbon from austenite which forms at Ac_1 into the



proeutectoid ferrite and then transformation of the ferrite to austenite. It differs from the view, often taken of the progress of the transformation, in which the proeutectoid ferrite transforms to gamma iron and is then carburized by migration of the carbon from the austenite which it envelopes. After all is it not the presence of carbon which causes the alpha iron to transform into gamma iron at the lower temperatures? Pure ferrite does not change to gamma iron until a temperature of 1670 degrees Fahr. (910 degrees Cent.) is reached. Carbon must be present in the ferrite in order to lower the temperature of transformation. Therefore, it seems logical to suppose that carbon enters the ferrite first and the transformation to austenite follows afterwards. Now—if the solubility and the rate of diffusion of carbon in the ferrite has been reduced by the presence of aluminum the ferrite envelope around the austenite grains transforms to austenite very slowly. As a matter of fact, the evidence presented by the photomicrographs of aluminum-bearing carbon steels indicate that the proeutectoid aluminoferrite may remain untransformed up to temperatures far above the theoretical Ac_3 temperature of the steels investigated. If such an envelope of body-centered cubic crystals of ferrite surrounding the face-centered cubic crystals of austenite persisted it would prevent growth of the latter.

While aluminum would raise the Ac_3 point as described, it would also have the effect of raising the Ar_3 for a given rate of cooling, as it is known to do. The persistence of very low carbon austenite or of aluminoferrite around each

of the crystals of austenite would cause transformation to alpha iron to commence early at grain boundaries during cooling and increase the "critical rate" of cooling for the steel containing aluminum. The shallow-hardening effect is thus accounted for.

If the foregoing suggestion be sound, then aluminum does not act so much to produce fine grain as it does to cause a maintenance of the grain size initially imposed on the steel, and it should therefore be as difficult to refine the grain of an aluminum-bearing steel which had been coarsened by high temperature exposure as it is to increase the grain size which has been made relatively fine in the rolling process. The difficulty of attaining intermediate grain sizes would result from the fact that it requires the presence of only a relatively small amount of aluminum in ferrite to reduce materially the rate of carbon absorption and diffusion.

Experiments with an aluminum-bearing carbon steel of normally fine grain and the same steel on which a coarse-grain size had been imposed by high temperature exposure would be of value in determining the effect of aluminum on grain size and whether the barrier to grain growth of austenite is actually an envelope of body-centered alumino-ferrite surrounding the face-centered austenite crystals.

Written Discussion: By E. E. Thum, editor of *Metal Progress*, American Society for Metals, Cleveland.

Since so much of Mr. McQuaid's argument rests on the premise that the three heats have different quantities of the metal aluminum in solid solution but the same amount of aluminum oxide, it is to be hoped that he will give an appendix in the final publication showing how these analyses were made. Many have the idea that the chemical analysis of aluminum and alumina is rather difficult to make and to check.

His low aluminum heat is noteworthy in several aspects. In the first place, the recovery of aluminum is much higher than in the other two. Totaling the aluminum as such and the metal in the oxide, we find that 7 ounces gets into the steel out of the 8 ounces put into the ladle, a recovery of 87 per cent. In the medium and high aluminum heats the recovery is much lower, about 60 per cent each, 2-B-2 figuring to have 19.5 ounces of aluminum per ton of metal out of 32 ounces put into the ladle, and heat 3-B-3 recovering 28.5 ounces out of 48 ounces.

Now whether this has anything to do with the microstructure of the normalized samples after reheating to 1225 degrees Fahr. (665 degrees Cent.) for 24 hours (Figs. 2 to 11 respectively) or not, I cannot say, but the low aluminum heat, as Mr. McQuaid points out, appears to be a high carbon steel. This is untenable, on the basis of chemical analyses showing all three to have 0.36 to 0.38 per cent carbon. Mr. McQuaid (page 499) says that "one of the primary effects of the aluminum addition on steels heated at temperatures just below the critical range is to cause a retraction of the carbide from the boundary ferrite, thereby forming a larger ferrite mass free from carbon and also much heavier carbide at the pearlite boundaries." A little work with a planimeter, measuring the respective areas of ferrite and pearlite, shows that he is mistaken in this, and the exact opposite is true. The medium and high aluminum steels have pearlite with about the ordinary content of carbon—not

higher—and the low aluminum steel has an unbelievably low-carbon pearlite. The figures are:

Steel	Micros Measured	Area Pearlite Per Cent	Area Ferrite Per Cent	Carbon Content of Pearlite Per Cent
High Al	2, 5, 8	43	57	0.84
Medium Al	3, 6, 9	39	61	0.95
Low Al	4, 7, 10	87	13	0.44

In the highest aluminum steel of the three, the carbon content of pearlite (figuring all the carbon shown in the chemical analysis to be uniformly distributed in the pearlitic areas) is the nearest to what one would expect for a plain carbon steel. It might also be remarked that a hypothetical large solubility of carbon in aluminum-bearing ferrite would tend to reduce the relative area of pearlite, without necessarily changing its carbon content. At any rate, an abnormal pearlite or unusually wide rivers of ferrite cannot be explained on the basis of aluminum when the high aluminum steel is normal and the low aluminum is abnormal.

I have no explanation of why a 0.38 per cent carbon steel, low in alloying elements, should have such a low carbon content in the pearlite after a normalizing heat treatment and a spheroidizing anneal. To me this is more of a mystery than the action of the three steels on reheating to 1500 and 1700 degrees Fahr. (815 and 925 degrees Cent.) respectively for 15 minutes. At 1500 degrees Fahr. (815 degrees Cent.) the ferrite envelopes are still alpha iron (ferrite does not transform to gamma iron until 1670 degrees Fahr. (910 degrees Cent.) is reached) and the grain boundaries can only become austenite as the carbon diffuses outward from those portions of the alloy which were once pearlite. This diffusion takes time; how much time I cannot compute, but evidently 15 minutes is not enough for any of these alloys, even for the low aluminum steel with the thin ferrite envelopes. One can readily agree with Mr. McQuaid that austenitic grain growth is prevented by untransformed ferrite at the grain boundaries, and none of these steels coarsened after a short stay at 1500 degrees Fahr. (815 degrees Cent.).

(One notes that the low aluminum steel did coarsen in 15 minutes at 1500 degrees Fahr. (815 degrees Cent.) if it had not previously been given the spheroidizing anneal. To my mind that is not exactly proof that massive carbides dissolve at a different rate than a plate of carbide. The solution of a carbide particle into austenite must obviously be done by atoms of carbon breaking away from the particles of carbide and losing themselves in the surrounding iron. This is something which can occur only at the surface (interface). The ratio of surface to the mass of the particle is very large in the plates of carbide in pearlite, whereas the ratio of surface to mass is the mathematical minimum in a spherical particle. Hence the solution rate may be identical at a given temperature, but the time for disappearance of a carbon particle of given mass is much shorter for a plate than for a spheroid.)

At 1700 degrees Fahr. (925 degrees Cent.) the conditions are considerably different, for the low carbon ferrite has at that temperature transformed into gamma iron, and the diffusion of carbon into what was once ferrite should be much faster, not only because of the great capacity of gamma iron to take

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carbon into solution, but also by the enhanced osmotic pressure of the added temperature. Even yet the reaction takes time, and if one assumes that austenitic grain growth is badly hampered until the carbon is fairly evenly diffused throughout the austenite, one can see that 15 minutes at 1700 degrees Fahr. (925 degrees Cent.) was not enough time for the high aluminum heat (Fig. 17) with its wide rivers of ferrite in the original network, but was enough time for the medium aluminum heat (Fig. 18) with its equally wide ferrite rivers, and for the low aluminum heat with its ferrite rivers hardly half as wide.

If you rule out the low aluminum heat on account of its inflated pearlite grains, and compare the medium and high aluminum heats, whose annealed microstructures are equivalent and what would be expected, it can be concluded that Figs. 17 and 18 constitute some good evidence that aluminum in austenite slows down the diffusion rate of carbon at temperatures above A_3 . This might be expected theoretically on the basis that aluminum is a large atom, and when it replaces iron atoms in the austenite (substitutional solid solution) it will fill up some of the open spaces and make it rather more difficult for the carbon atom to slip through—that is, dissolve and diffuse.

Mr. McQuaid, in his 1935 Campbell Memorial Lecture and in this paper, holds to the belief that it is metallic aluminum in solution rather than sub-microscopic particles of aluminum oxide that is of most importance in controlling the grain size of heat treated steels. He states that this is due to its effect on the carbide solubility in austenite and the transformation temperature. I would like to suggest that a little aluminum does not affect the equilibrium conditions so much as it does the rates of reaction and rates of solution and precipitation. Bear in mind that true equilibrium is attained only after a long time—impossibly long for practical production. He has demonstrated that carbon goes into solution more slowly in a high aluminum austenite than in a low aluminum austenite. It is a fair assumption that if carbon goes into solution with great reluctance, it will come back out with great celerity. Is not this fact alone sufficient to explain many of the observed phenomena concerning grain size, grain growth, and hardenability?

Written Discussion: By R. L. Wilson, metallurgical engineer, Timken Steel and Tube Company, Canton, Ohio.

Mr. McQuaid has prepared an excellent paper on the effect of aluminum on the quenched structure of steel for a definite condition of the material prior to quenching. While in such investigations there is sometimes difficulty in recognizing cause and effect, nevertheless our information on grain size and hardenability of steel has been increased by this work.

The observation has been made that in a medium carbon plain carbon steel normalized by air cooling from 1800 degrees Fahr. (980 degrees Cent.), the proportion of pearlite for ferrite in the structure seems to decrease with increasing aluminum content in the metal between the limits of 0.011 and 0.075 per cent. Figs. 2 to 10 inclusive show various microstructures to support this view. As the carbon content by chemical analysis was found to be essentially the same in all three steels, the difference in the appearance of the structures may be explained by supposing a pearlite richer in carbon in the higher aluminum steels, a difference in the type of carbide formed in the presence of alu-

minum, or a carbide of the same nature existing in different forms depending upon the aluminum content of the steel.

Even by theorizing with recent literature as a background, it is rather difficult to imagine that a difference in the aluminum content between two steels of the order of 0.06 per cent should make a notable change in the eutectoid carbon concentration of the steel or the carbon content of whatever complex carbide may be formed. On the other hand, if it seems more likely that the appearance of the pearlite depends upon the form of the carbide in the grains as influenced by the aluminum content of the steel, then the relation of structure to aluminum content parallels the effect of McQuaid-Ehn grain size on pearlite for the conditions described. In normalized fine-grained steel, for example, the carbide tends to be spheroidal and the pearlite grains are smaller than in coarse-grained steels of the same carbon content. The coarse-grained steel may also exhibit large pearlite grains similar to those shown for the low aluminum steel in Mr. McQuaid's paper. In either case the attenuation of carbon in the large grains could be ascribed to the size and distribution of the carbide particles. May we not ask, therefore, whether these qualities of pearlite are due to McQuaid-Ehn grain size rather than aluminum content? Or to the effect of aluminum content on the McQuaid-Ehn grain size?

Judging from experiences in the commercial manufacture of steels to controlled grain size, there appears to be a critical addition of aluminum that will produce a fine-grained steel. Either larger or smaller additions in the same circumstances leave the steel coarse-grained. If other steels of still higher residual aluminum content had been examined in this series of tests, and had shown a further decrease in the proportion of pearlite to ferrite, the preference would be stronger for the conclusion that the structural changes were caused by the aluminum in the steel.

Written Discussion: By R. H. Harrington, research metallurgist, General Electric Co., Schenectady, N. Y.

The general conclusion that coarsening of the carbide particles, particularly at the boundaries of pearlitic areas, affects the diffusion conditions for the carbide solution necessary for "normal" hardening conditions seems to be amply justified and this author, as usual for him, is to be complimented for another example of excellent research.

The writer would like to call attention to the photomicrographs in Figs. 2 through 7. Considering Figs. 5, 6, and 7 we see the structures of steels of 0.36, 0.37, and 0.38 per cent carbon content, differing chiefly in the amounts of dissolved aluminum, 0.075, 0.050, and 0.011 per cent respectively. The heat treatment applied as described in the paper should, one might expect, result in the formation of pearlitic areas proportional to the amounts of carbon available to form carbide, this proportion being slightly decreased by the coarsening of boundary carbide particles with increase in the amount of dissolved aluminum. Since quenching from 665 degrees Cent. (1230 degrees Fahr.) will retain about 0.06 per cent carbon in solution, there remains, in each of the three steels, about 0.30 per cent carbon to form carbides. The pearlitic areas should, therefore, occupy about 35 per cent of the total area. Visual examination leads to the conclusion that Figs. 5 and 6 show the structural ratios to be expected. However, Fig. 7, containing the least amount of dissolved aluminum

and therefore more nearly representative of a plain carbon steel, shows an apparent pearlitic area far in excess of the expected ratio. Since this alloy is really the base for comparison of the effects of increasing amounts of aluminum in solution, the writer feels that this apparent discrepancy in structure should be accounted for.

Considering also the present paper by Brophy and Parker relating to the effects of aluminum additions on the structures obtained by subsequent carburizing, the writer is led to the following conclusions: (1) aluminum in solution in carbon steels affects the boundary structure of pearlitic areas; and (2) the presence of alumina affects the internal structure of pearlitic areas, both factors combining in causing differences in behavior toward various heat treatments.

Written Discussion: By B. L. McCarthy, metallurgist, Wickwire Spencer Steel Co., Buffalo, N. Y.

Mr. McQuaid has, in this paper, presented some very interesting thoughts on the importance of carbide solution and diffusion. Experience has shown that too little importance has been attached to these features in the past. Exhaustive studies on the rate of solution of both ferrite and carbide particles in connection with the patenting treatment have shown that wide variations can exist. The tendency for some steels to develop large particle size of both carbide and ferrite and to present problems on rate of diffusion, is not confined to aluminum alone. Steels which have come to my attention to which no aluminum has been added have shown marked variations in rate of solution in patenting, employing identical deoxidation procedures.

The manner in which Mr. McQuaid has traced the influence of aluminum to the hardening characteristics leads the way to further study of inherent characteristics other than grain size and the question arises as to which is first, the grain size and its influence on reaction rates or the tendency toward slow solution and diffusion and its effect on grain growth. The fact that additions of aluminum to steel must be great enough to produce a residue before grain refinement, as determined by the McQuaid-Ehn grain size test, is effected, makes one wonder if the refinement is because of a fine dispersion of Al_2O_3 or because of the influence of aluminum in solution.

While the influence of aluminum is clearly shown, I believe that this is only a part of the story which, when completed, will include a number of elements, some of which are not listed as present in the analyses of steel.

The actual influence that these elements have on the particle size must be more clearly established. Obviously there is some delay in the transformation of austenite to pearlite which permits of some solubility of carbide in alpha iron combined with a faster reaction rate than would be anticipated. Some samples of steels to which no aluminum has been added seem to show a tendency toward the formation of coalesced particles of carbide rather than thin plates. This would increase the amount of carbide that could be contained in a pearlitic grain, accounting for the apparent increased amount of free ferrite and the slower rate of solution and diffusion.

There is every reason to believe that a continuance of this study and the influencing factors will reveal the reasons for inherent characteristics of steel not accounted for by the McQuaid-Ehn grain size alone.

Written Discussion: By Bertrand S. Norris, Pennsylvania State College, State College, Pa.

Among the many interesting observations stated in this paper, the one concerning the different amounts of ferrite present in the three steels after tempering at 1225 degrees Fahr. (665 degrees Cent.) is of particular interest. However, it is difficult to see how the coalescing of lamellar pearlite adjacent to the ferrite could produce so much ferrite. A question arises as to the relative amounts of ferrite present in the steels subsequent to the normalizing treatment. If the same relationship existed after normalizing as was true after tempering, the difference in the amounts of ferrite might have been produced by difference in the austenite grain size at the normalizing temperature. McBride, Herty, and Mehl have clearly shown (in a recent paper before this society) that the size of the austenite grains has a profound influence upon the amount of ferrite precipitated during the cooling from a normalizing temperature. The amount of ferrite formed increases with decrease in austenite grain size. Thus, if the high aluminum steels had a smaller grain size than the steel with a small amount of aluminum, the former would have produced more ferrite during the cooling from the normalizing temperature. This in turn would still be evident after the tempering treatment.

When the three steels were tempered and subsequently heated at 1700 degrees Fahr. (930 degrees Cent.) the hardness penetration was very much greater for the low aluminum steel than for those containing large amounts. This difference was assumed to have been caused by the greater number of carbides present in the high aluminum steels. It would be interesting to know whether the high aluminum steels hardened to a shallower depth when all of the carbides had been dissolved in the austenite prior to quenching. Since all of the steels have practically the same alumina content, it would be possible to see to what extent the presence of aluminum influenced the hardness penetration.

Written Discussion: By Sydney Nashner, Underwood Elliot Fisher Co., Hartford, Conn.

Mr. McQuaid's paper is an interesting contribution to further our knowledge concerning transformation reactions in steel. The possible effects of carbide size and diffusivity on grain growth and hardenability are well presented.

One phase of this paper, however, seems to be open to some discussion. Referring to Figs. 5, 6, and 7, which represent 3B3, 2B2, and 5B3, after the 24-hour hold at 1225 degrees Fahr., it is seen that the arrangement of ferrite and pearlite areas is such as to lead one to the conclusion that the structure in Fig. 7 was formed from coarser-grained austenite than is the case in either Figs. 5 or 6, Fig. 5 representing the finest of the three. This conclusion assumes that the subcritical heating has not altered the possibility of determining previous austenitic grain size, i.e., that existing at the normalizing temperature, from the ferrite-pearlite structure. Fig. 7 shows what appears to be characteristic ferrite envelopes formed as a result of transformation at austenite grain boundaries thus marking them out. The more numerous pearlitic clusters in Figs. 5 and 6 indicate that more austenite grains probably existed in the given area, that is, the austenitic grain size was smaller. Actual proof of these conditions is bound up in the structures which existed after nor-

malizing and prior to the 24-hour 1225 degrees Fahr. heat. These structures compared with the ones observed after the subcritical heat would show what changes were brought about by it. Unfortunately the structures of the three steels investigated as they existed after normalizing have not been included in the paper.

Assuming that different austenitic grain sizes did exist in each of the three steels at the normalizing temperature, it is then possible that the coarser carbides and larger amounts of ferrite are due to the higher transformation rate resulting from the presence of more austenitic grain boundaries where nucleation may take place. This is in keeping with the abnormal tendencies of steel cooled from fine-grained austenitic condition. The subcritical anneal would tend to amplify this condition without changing the relative status of carbide and ferrite size in the three steels. The differences in rate of solution and diffusion as observed by Mr. McQuaid later in his paper would follow from the differences in carbide and ferrite size as explained in this paragraph.

It is apparent in this discussion that aluminum has been given the role of austenitic grain growth inhibitor (as the oxide) rather than an alloying element directly affecting carbide size and amount of ferrite. It is interesting to note that the heat with the lowest aluminum additions has resulted in what is apparently the larger austenitic grain size. It seems as though an investigation into the structures resulting from equal austenitic grain size and cooling rates for the three steels would throw some light on the question of how much credit can be given to aluminum as an alloying element, and how much to grain boundary nucleation. It would be interesting to know whether Mr. McQuaid has this information for us.

Written Discussion: By L. F. Lottier, assistant metallurgist, Peoples Gas, Light and Coke Co., Chicago.

That the effect of aluminum in plain carbon steels is to stabilize the carbide is very forcibly brought out in the paper. That this stability is made possible by the aluminum being present in the ferrite, or by the formation of a special carbide is not argued, although it is mentioned in the abstract that the effect is likened to a similar effect produced by oxygen as FeO in solution in ferrite.

The study of cast iron, while it has always been considered simple when compared to steels, is probably more complicated than our plain carbon steels. It is now quite well known that copper acts in a way similar to nickel in grey iron in amounts up to about 1.00 per cent, but that when quantities are added to bring the analyses between 1.50 and 2.00 per cent, a rapid toughening is noticed. It is evidenced as both a reduction of graphite flake size and consequent resistance to free machinability, although part of the toughness may be attributed to the copper in solution in the ferrite. Melland and Waldron,* as early as 1900, investigated the effects of aluminum in cast iron, and although the results were somewhat variable, they found that up to 0.50 per cent, aluminum acted as a graphitizer, but in excess of this figure apparently the stability of the carbide was increased, and excessive graphite precipitation was arrested.

**Journal, Iron and Steel Institute*, 1900, Vol. II (British).

I believe that at the present time it is the contention of most metallurgists that in the formation of graphite the formation of massive cementite precedes the graphite precipitation; that is, when the metal is in the solid state. From this end, it seems plausible to reason that where no excess carbon is present and where no graphitizers exist in any quantities, such as are found in cast iron, aluminum in steel tends only to increase the stability of the iron carbide. In other words, the small quantities of aluminum—say 0.05 per cent—do attempt to carry out their graphitizing so strongly that the resultant carbides are extremely stable. The action stops here, of course, for there are not enough graphitizers present, such as silicon, to again break down the iron carbide into graphite and ferrite, the result being an iron carbide with a strong tendency to remain fixed and permanent.

Oral Discussion

T. G. HARVEY:¹ I should like to ask Mr. McQuaid if increasing the aluminum content from one-half pound per ton to two or three pounds per ton will increase the machinability?

My experience has shown me that in 0.50 per cent carbon, chromium-molybdenum steels of practically the same carbon content, the steel showing the larger proportion of ferrite apparently has better machinability than the one having the smaller amount of ferrite.

The steel showing the larger percentage of ferrite is similar in microstructure to the steel Mr. McQuaid showed containing 2 to 3 pounds of aluminum per ton and the steel showing the smaller percentage of ferrite is similar in microstructure to the steel Mr. McQuaid showed containing one-half pound of aluminum per ton.

R. F. MEHL:² The papers by McQuaid, by Zimmerman, Aborn, and Bain, and by Brophy bring so very many points of interest, that discussion and argument could go on interminably. But one point of frequent confusion at least should be mentioned, particularly since some of Mr. Thum's remarks suggested it, and because Dr. Shapiro's comments were on it, and particularly because it should be borne in mind in reasoning about the types of pearlitic structure observed by Mr. McQuaid.

It must be repeated again, that the occurrence of a pearlitic structure in unalloyed iron-carbon alloys is not proof of the carbon content of the alloy, for a unique carbon content at the eutectoid point in the iron-carbon system exists only under equilibrium conditions. At any finite rate of cooling the pearlitic structure may be realized over a range of carbon composition. Recent work by Dr. Wells in my laboratory on high purity iron-carbon alloys shows that this composition range of the pearlitic structure is as high as 0.15 per cent carbon at rates of cooling as low as 2 degrees Cent. per minute, and that the range would doubtless be greater at faster rates, though not in direct proportion to rate. The paper by Professor Upton of Cornell, printed in the *TRANSACTIONS*³ several years ago, presents the matter with great clarity.

¹Snap-on Tools, Inc., Kenosha, Wis.

²Director of the Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh.

³G. B. Upton, "The Habits and Laws of Decomposition of Supercooled Solutions with Special Regard to Austenite," *TRANSACTIONS*, American Society for Metals, Vol. 22, 1934, p. 690.

From this we may see that all planimetric methods for estimating carbon from the relative areas of pearlite and ferrite are quite fallacious. We conclude, therefore, that the occurrence of pearlite is largely influenced by rates of cooling and the accompanying super-cooling effects, and we may see that differences in deoxidation, in alloy content, and perhaps in prior treatment should exert an appreciable effect on the character of the pearlite found and on its carbon content.

I should very much like to express my satisfaction in Mr. Brophy's work. Carburization is such a fearfully complicated process that understanding can only come by performing relatively simple experiments under very carefully controlled conditions, as Mr. Brophy has done—scientifically speaking, much of the published work on carburization has little meaning.

O. E. HARDER:⁴ I consider it unfortunate that Mr. McQuaid did not show the microstructures of these three steels in the normalized condition before he subjected them to the spheroidized condition for twenty-four hours at 1225 degrees Fahr. In other words, from there on, we are talking about a material, the original condition of which we do not know. The heating experiments in which he transferred specimens from the low temperature annealing furnace to the furnace at 1500 degrees Fahr., and held them for fifteen minutes, need some discussion, in my opinion. If you place a thermocouple in the center of a specimen of the type that he used, and follow the heating curve, our experiments indicate that it will not get to this temperature of 1500 degrees Fahr. in less than ten minutes, and that it is at this temperature only five minutes. This is a very short time for the solution and diffusion reactions to be completed. The next thing I would like to say (using the various diagrams by Foley and Mehl) is that when we come to the lower critical range, the pearlite goes into solution and forms austenite. It is rather difficult for me to understand the mechanism which they propose that the carbon then diffuses into the ferrite, because the solubility of carbon in ferrite is very low. May I suggest that the mechanism is quite different from that, and that the ferrite goes into the solution in the austenite. I think that the ferrite grains which are left in Mr. McQuaid's specimens show quite clearly that they are being corroded, or being put into solution by the austenite with which they are in contact. Also, I think that makes a satisfactory explanation because you have ferrite going into the outside of the austenite grain, and, therefore, keeping the carbon content low in the outside of the grain.

The next point I want to make is with reference to the carbide not being in solution in these hypoeutectoid steels, and therefore, modifying grain growth. So far as I can tell from looking at the photomicrographs there is no evidence in any of these pictures that there are carbides not in solution. I think they did go into solution and that the material that is not in solution, and the thing that inhibits grain growth, is undissolved ferrite.

Another point I wish to make is with reference to Steel 5B3. If you look at the microstructures in those pictures and determine the amount of ferrite, it shows 11 per cent of ferrite, and on that basis, it would mean that the carbon content of the pearlite shown in that specimen is about 0.43 per cent. This

⁴Assistant Director, Battelle Memorial Institute, Columbus, Ohio.

is an unusually low carbon content for pearlite. As Dr. Mehl has pointed out, selected rates of cooling might bring about that effect, and it would, therefore, be of some importance to know if there was an unusual rate of cooling 5B3 as compared with the others, or if in the selection of the area in the photograph, it is not truly representative of the specimen. There is another thing that might be pointed out—without going into great detail, it is rather obvious from the photomicrographs that 2B2 has a coarser grain structure than 3B3. This difference in the original grain size of 3B3 and 2B2 may help in accounting for some of the results obtained by the author of this paper.

H. W. McQUAID: I am very much interested in what Mr. Thum had to say. This question of measuring, or determining the carbon in the pearlitic area by planimeter measurement, is to me difficult to understand. Dr. Herty discussed that, several years ago, when he indicated that the appearance of a carburized case under the microscope was not a true indicator of the depth of carburizing, and one could be mistaken by thinking that because it looked like a 0.15 or 0.20 per cent carbon steel, that that was correct. As a matter of fact, what looked like a 0.20 or 0.30 per cent carbon might have been 0.40 or 0.50 per cent. The only reason I analyzed these pieces was not because the low aluminum steel looked high in carbon, but because the high aluminum steel looked low in carbon.

I have these structures for the benefit of Dr. Harder at 100 diameters in a normalized condition and they indicate exactly what I would expect to see. That is, the high aluminum showed a typical 1800 degrees Fahr. slow cooled structure, pearlite fine, apparently a considerably greater amount of ferrite than in the normal coarse grain type, slowly cooled from 1800 degrees Fahr.

The questions of the time of heat, etc., the rate of cooling, etc., are, of course, interesting. These pieces were all quenched from 1225, 1500 and 1700 degrees Fahr., consecutively in the same bath. The rates of cooling were approximately the same, and very fast. The time at temperature of 15 minutes is not an unusually short time in commercial practice. 1040 steels in usual continuous furnace practice are seldom heated more than 10 or 15 minutes.

I was interested in what Dr. Harder said about the ferrite dissolving in the austenite rather than the ferrite transforming to austenite progressively as the carbide dissolved. We know that carbide at temperatures above the A_{c1} will dissolve in ferrite to a certain extent, enough to start the rearrangement of the crystal lattice so that it can become austenitic.

Mr. Harvey asked a question which is interesting to me, and that is the effect of aluminum content on machinability. That is a subject upon which we could talk for the next hour and probably not get far, because usually the aluminum addition makes the steel tougher, and it is not easier to machine than the lower aluminum type. On the other hand, whether or not high aluminum steel machines easier than low aluminum steel, depends upon the temperature at which you treat it. If you are talking about maximum machinability, you must be talking about temperatures—temperatures above the grain coarsening range, and when you are talking about that, it is my opinion that when aluminum steels are properly coarsened, they will machine better than

the low aluminum steels at lower temperatures. However, as a rule, under normal conditions, the finer grain, or aluminum-treated steels, do not machine as well as the coarser grain type and require a higher normalizing temperature to put them in that condition, but if the temperature is high enough, the difference in machinability is very little. It is more a question of structure of the pearlite in my opinion than it is the amount of ferrite, or the amount of aluminum present.

I am gratified at the discussion that has taken place, and it was for that reason that this paper was presented.

Author's Closure

It is pleasing indeed to see the interest that this paper has developed, and the author wishes to thank those who have taken of their time to present discussion.

The principal object of this presentation was to indicate the difference in structure which is found when steels of approximately the same commercial specification but varying in the aluminum addition are treated under the same conditions. The three steels described were as close to being commercially identical as is normally possible and their treatment was as nearly identical as possible. There should be no appreciable difference in heating or cooling rates between the three samples, since in every case they were cooled by quenching in water and heated together side by side in the same furnace. For this reason, the question of variation in cooling rates, temperatures, etc., it is believed, can be eliminated from the discussion and we can confine our whole attention to the differences found in the behavior of the different heats and the possible reason for such differences. The original intention was to compare three steels to which different amounts of aluminum had been added after identical practice from the ingot down. It is to be regretted at this time that instead of normalizing at the same temperature of 1800 degrees Fahr., these steels were not all brought to a uniform austenitic grain size prior to treatment by normalizing at approximately 2000 degrees Fahr., which in these steels should be above the grain coarsening range. This was not done because of the well known fact (in practice) that the effect of the initial austenitic grain size after rolling or forging is usually eliminated upon reheating through the critical range. Thus the shallow hardening and deep hardening types of steel regain their characteristics when reheated even after a previous normalizing at temperatures as high as 2300 degrees Fahr. If this were not true, all forgings which are not annealed should behave as coarse-grained, deep hardening steels when heat treated and we, of course, know that this is not the case. As Dr. Harder, Mr. Nashner and others have indicated, it would be of interest to check the effect of holding at temperatures just below the A_{c1} , steels which were of approximately the same austenitic grain size but which varied in the amount of aluminum addition. Such an investigation is now in progress.

Mr. Foley's views are naturally of interest to the author and are much appreciated. His suggestion that fine grain steels should be difficult to refine after being coarsened does not check with actual experience. The aluminum-treated steels are not usually made fine by the rolling process, which, as a rule, is conducted at a temperature in excess of the grain coarsening range.

Aluminum-treated steels after being coarsened by a high temperature treatment regain their fine grain on reheating. In order to refine the grain of a coarsened fine grain steel, it is necessary to cool below the critical range and reheat. This requirement in itself is evidence that the inherently fine grain steels are only so by some effect connected with the critical range changes on heating. It indicates that the presence of nonmetallic nuclei are not a primary factor in the grain growth except in their connection with size of the initial austenite grain. That they do play some part is, of course, possible, although it is believed that the effect may be one of decreasing the interface bond between the carbide and the ferrite as it is formed on cooling. This would have the same effect as an increase of surface tension of the carbide and a resulting tendency to coalesce.

The possibility of the effect of dissolved elements such as aluminum, copper, etc., as well as FeO and other oxides on the surface tension of the freshly formed carbide, should not be overlooked and the persistence of an interface constituent which interferes with the solution of the carbide on heating may explain some of the effects of additions to the ferrite.

The discussion of Mr. Harrington is appreciated and his doubt as to the structure of the low aluminum steel as being representative is probably in order. As stated in the paper, actual chemical analyses were made of micro-sections and all three specimens are within two points of carbon. To the author the appearance of these three steels at 100 diameters (now shown) is unusual only in the higher aluminum types and in the lower aluminum steel (Fig. 7) is as would be expected after an 1800 degrees Fahr. normalize. The higher aluminum types apparently were lower in the percentage of pearlite than would be expected from a normalized S.A.E. 1040 steel. It is the opinion of the author that the discrepancy in apparent pearlite percentage is due to the aluminum effect on the carbide characteristics. The structures of the three steels in question are shown in the December 1935 TRANSACTIONS of the A.S.M. on page 811, Figs. 3, 5, and 6. Schane in the December 1934 TRANSACTIONS on page 1042 shows also typical structures of aluminum and non-aluminum treated S.A.E. 1040, normalized at 1800 degrees Fahr.

To the author, who has from time to time had to examine many microstructures of as rolled and normalized coarse-grained S.A.E. 1040, the structure shown in Fig. 7 does not look particularly unusual, but rather the structures shown in Figs. 5 and 6.

The discussion by Mr. Thum touches on the same point as Mr. Harrington's, that is, the apparent discrepancy in the pearlitic structure. It is evident that the planimeter method of determining pearlitic carbon content fails when applied to steels of the same carbon content but of varying carbide structure and distribution. It certainly can only be correct for one specific degree of pearlite divorcement and will vary with the fineness of the carbide in the pearlite and the degree of coalescence. Certainly one would not expect to check the carbon analysis by a planimeter measurement of the apparent pearlitic areas unless the thickness of the carbide plates and the distance between them were known (or constant). In the author's opinion the apparently low carbon content of the coarse-grained (low aluminum) pearlite is evidence of the relative attenuation of the carbides in this type of steel and hence an indica-

tion of the greater surface area in contact with the ferrite. This in itself offers an explanation of the increased speed of solution of the carbide.

The author has deliberately tried to avoid the use of the numerical results obtained in the analysis of these steels for metallic aluminum. It must be remembered that no guarantee is offered for the final accuracy of the aluminum analysis, although the results given are the values obtained by two laboratories which checked rather well. The initial charge also contained some aluminum and the discrepancy between the calculated recovery and the analysis may be due to some aluminum from the charge. The original charge was 100 per cent very low carbon scrap and in the melting (electric furnace) no oxidation period was necessary.

Mr. Thum's criticism of the use of the word "rate" to indicate relative speeds of solution of the different types of carbide solution is well taken, although the author had in mind the rate of solution of the carbide as a whole and not the rate of solution of a given area of carbide interface.

It is interesting to speculate on the suggestion of Mr. Thum's that since the carbide goes into solution in the aluminum-bearing ferrite, it also must come out with greater celerity and hence accounts for the decreased hardenability of the aluminum-treated steel. Also, since (it is believed) grain growth takes place only when complete carbide solution and diffusion has taken place, the coarse-grained steels will naturally harden better and deeper than the finer grained steels. This, following out Mr. Thum's suggestion, would be the result of the greater stability of the solution of the coarser grained steels with no boundaries of lower carbon content and hence high transformation temperature. By the same reasoning, any addition to the ferrite which reduces the carbide solubility must decrease the hardenability providing quenching takes place from a temperature below that of complete carbide diffusion. Also, it might be argued that an increase in the ferrite solution addition, be it metallic or nonmetallic (FeO) to the point where the effect on the carbide solubility is almost as great in the center of a pearlite grain as it was in the boundary, will eliminate the grain growth inhibition. Thus an increase in aluminum beyond a certain maximum may remove the grain refining effect of the reluctantly soluble carbides.

Dr. Harder's suggestion that there is no indication of the carbides not being in solution at temperatures above the A_{c3} is certainly correct, although we have some indication from the sodium picrate etch that carbides are still out of solution as shown in Fig. 27. There are, however, many indications that there exists a very heterogeneous austenite caused by incomplete diffusion of the carbides which have gone in solution. The suggestion that it is the undissolved boundary ferrite which inhibits grain growth, seems to me to be another way of saying the same thing that Mr. Thum has indicated. In other words, low carbon boundary ferrite or perhaps carbonless ferrite in the grain boundaries results in boundaries which have an exceedingly high transformation rate and hence, not only is the grain size preserved through the heating and quenching, but the properties of the quenched piece are greatly affected as well.

Mr. Wilson's comments are of special interest and reflect the reaction of one who has had long and intimate connection with the making and handling of aluminum-treated steels. There is no doubt but what the attenuation of

carbon in the large grain can be ascribed to the size and distribution of the carbide particles. Whether the carbide characteristics in the three steels are due to aluminum or to the grain size itself is a question which seems to be logically answered in one way only. The carbide characteristics cannot primarily be due to grain size or the aluminum-treated steels would not show the expected hardenability results when reheated for hardening after a normalizing from above the grain coarsening temperature. The aluminum is added to produce, under the right conditions, a steel having a small McQuaid-Ehn grain. The difference between the effect of low aluminum and high aluminum addition is one primarily of coarsening temperature range, of which the McQuaid-Ehn test is an indicator. The grain coarsening temperature, it is believed, is connected directly with the carbide solution and diffusion characteristics. Compare Figs. 12 and 17, 13 and 18, 14 and 19. The aluminum addition in some way has a powerful effect on the carbide stability at temperatures close to the A_{c1} point so that it is believed that the primary effect is on the carbide and the grain size effect is a secondary one.

The question of the effect of aluminum when added in large percentages is one which has bothered the author for many years. It is well known that increasing additions of aluminum do not result in increasing grain refinement beyond a relatively low amount. They do decrease the carbide solubility and require increasingly high temperatures for complete carbide solubility. There is a maximum grain refinement effect at relatively low aluminum content but the carbide solubility decreases as the aluminum increases and higher temperatures are required until the point of actual graphitization is reached. Mr. Harrington's suggestion that metallic aluminum effect is primarily a grain boundary effect, while the aluminum oxide effect is uniformly felt throughout the grain, is one which should, I believe, be given careful consideration. The effect of submicroscopic alumina on the stability of carbides within the grain may be an important factor in increasing the surface tension of the carbide with a resultant decrease in coalescence rate and perhaps solubility in the austenite.

It is possible that the grain size refinement effect reaches a maximum when the carbide coalescence reaches a maximum in the boundary of the pearlite grain as compared to the center and then decreases, as the pearlite becomes more coarsely lamellar.

Mr. Lottier's comments are appreciated and it is believed are sound. The close connection between the effects of the aluminum addition and the silicon addition is evident to anyone who has investigated their combined results.

In Mr. Norris' discussion he brings up the same point as previously discussed in regard to the original austenitic grain size. It is interesting to speculate as to why the amount of ferrite formed increased with decreased austenitic grain size. This is undoubtedly true in the same steel, but when we are comparing steel of two different types, we immediately enter into uncertain ground. Thus we might take steel of identical treatment and grain size and try to explain why the coarse-grained normal steel has less ferrite in the boundary than a coarse-grained very abnormal steel of approximately the same analysis. Coarse-grained abnormal types are not common, but still there have been many cases where such structures have been found to exist. Con-

versely, steels of the fine-grained, normal type, with apparently much less ferrite out of solution, are quite common and we have some difficulty in comparing these with steels of the fine-grained, abnormal type and arriving at the conclusion that the grain size itself is an important factor in the amount of ferrite precipitated. In fact, the reverse may be the case, that is, the grain size may be related to the amount of ferrite precipitated.

It is not believed that the paper indicated, as assumed by Mr. Norris, that the difference in hardenability was caused by the difference in the carbides present in the high aluminum steel. As a matter of fact, it is not believed that there is any difference in the amount of carbides present in these three steels but only in the physical size and distribution of the carbides. There is no doubt but what the hardenability of the three steels discussed would be the same providing a sufficiently high temperature was used to insure a complete solution of all the carbide and a uniform austenitic structure prior to quenching. This can be obtained by sufficiently high temperature and enough time to permit equalization of the carbon in solution throughout the austenite.

THE DIFFUSION OF HYDROGEN THROUGH NICKEL AND IRON

BY W. R. HAM

Abstract

The diffusion of hydrogen through nickel and iron has been found to follow the general equation derived from kinetic theory on the assumption that diffusion is chemical in nature.

The linear relation between $\log D$ (diffusion rate) and $\log P$ (gas pressure) at constant temperature for the pure metals shows a slope of 0.5. When the metals have not been degassed or contain certain other elements such as carbon or nitrogen in solution the slope of the isotherms is greater than 0.5, and the increase in slope appears to be approximately proportional to the amount of foreign element in the metal.

A similar linear relation exists between $\log D$ and $\frac{1}{T}$ (where T is Abs. Temp.) so long as no phase change (crystal structure) or electronic change (e.g. magnetic) occurs. In such regions the isobars undergo a marked change in slope.

With nickel and iron the magnetic change at about 360 and at 750 degrees Cent. respectively are clearly defined by diffusion data. In addition, iron exhibits changes in the isobars at 945, 900 and at between 200 and 350 degrees Cent. A definite difference in temperature is observed between Ar_3 and Ac_3 and this appears to be a true hysteresis.

The other points are all ascribed to electronic changes of the iron atom and it is suggested that the well known maximum in the tensile value of iron at 200-350 degrees Cent. is explained in part by one of these electronic shifts.

The general conclusion is reached that the isobars from hydrogen diffusion tests furnish an accurate means of tracing phase or electronic changes in iron and nickel, and that the change in slope of the isotherms provides a means in some instances of determining small amounts of foreign elements in solution in the metals.

A paper presented before the Eighteenth Annual Convention of the American Society for Metals, Cleveland, October 19 to 23, 1936. The author, W. R. Ham, is associated with the department of physics, Pennsylvania State College, State College, Pa. Manuscript received June 1, 1936.

DISCUSSION of all the work of various observers on diffusion and solution of gases in metals would be so extended as to be quite beyond the scope of this paper. The literature is most voluminous. Most of the references on solubility experiments for gases in metals are cited in the *Sorption of Gases by Solids* by McBain (1).¹ The recent Annual Institute of Metals Lecture by R. F. Mehl (2) on "Diffusion in Solid Metals" gives a very sound and complete resume to date of both theoretical and experimental progress along the line of internal diffusion.

Working back from these two references alone, a rather complete bibliography of the more important discussions and researches can be developed.

Of the earlier work, that of O. W. Richardson (3) on diffusion of hydrogen through platinum is considered classical, as is also the work of Johnson and Larose (4) on diffusion of oxygen through silver. The thermodynamics of the latter work has been considered by J. H. Simons (5).

The literature until recently did not settle the nature of the diffusion process, whether physical or chemical, whether through the lattice or along grain boundaries or through Smekal cracks; however, the work of Smithells and Ransley (6) shows beyond argument that in hydrogen diffusion through iron, lattice diffusion only is involved. That various other types of diffusion may be encountered is indicated by Mehl in the paper cited.

Since the data given in the present paper indicate that hydrogen diffusion through the metals discussed is chemical in nature, a theory has been developed on this chemical viewpoint and is attached as an appendix.

EXPERIMENTAL TECHNIQUE

Before designing apparatus it is often best to see what conditions should be attained, and for this particular problem these conditions may be listed as follows:

1. Chemical and mechanical homogeneity of the diffusion diaphragm and complete freedom from gas leakage at the highest temperature of experimentation.
2. The diaphragm should consist of heavy sheet material (about 0.040 inch or more) in order to withstand severe treatment and to permit ready inspection.

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

3. It must not be contaminated in assembling.
4. Complete freedom from temperature gradients and maintenance of constant temperature to permit equilibrium before and during the interval that the diffusion rate is measured.
5. The method of measuring rates of diffusion of the gases should be so devised that gas pressure on the outgoing side may remain constant.
6. Provision to control and vary the gas pressure on the ingoing side of the diaphragm.

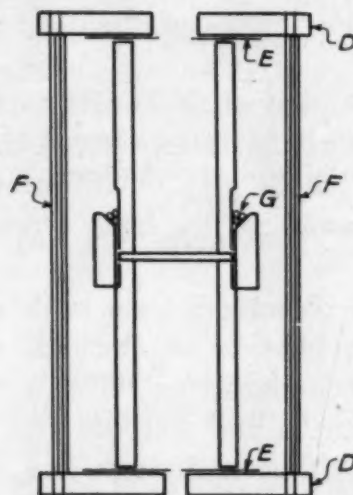


Fig. 1—Assembly of Diffusion Disk and Holder, Ready to be Placed in Hydrogen Atmosphere for Welding.

The assembly for diffusion through nickel and electrolytic iron is shown in Figs. 1, 2 and 3. In the nickel diffusor any trace of copper may be removed by washing with HNO_3 . The water-cooled nickel extension tubes are atomic hydrogen welded while hydrogen is passed on both sides of the diffusor. The arrangement of the diffusor at the center of the furnace (F in Fig. 4) eliminates longitudinal temperature gradients, and no radial gradient could be detected either by the optical or thermocouple method of temperature measurement.

Maintenance of a truly steady state during diffusion measurements has provided some difficulty. In the early tests (1929-32) a mercury manometer (M in Fig. 4) with a small rise of 1 to 2 millimeters and having electrical contacts was used, and measurements were made on the time required to close the upper contact, the volume

of the system being known; the time was measured automatically by an electrical clock (E).

A much simpler method (Fig. 5) consists in observing the pressure on the outgoing side by means of the McLeod gage. Since the pumping system is very fast, the gage shows a pressure proportional to the rate at which the gas passes through the diffusor, as this gas must also diffuse through the glass tubes to the pumps and especially

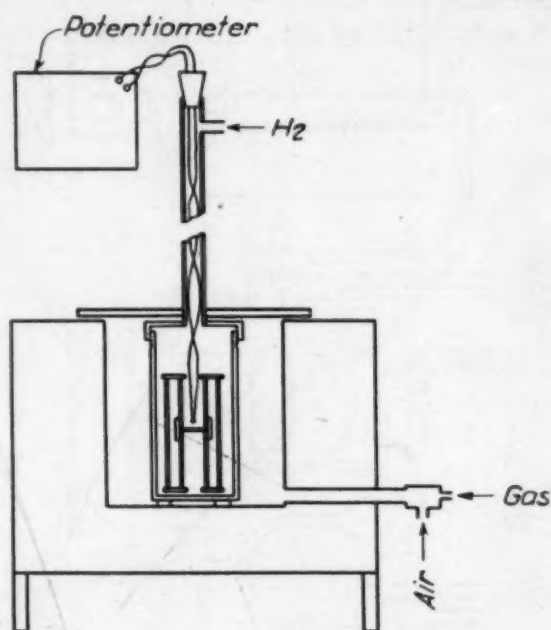


Fig. 2—Welding Furnace, Holder and Bomb.

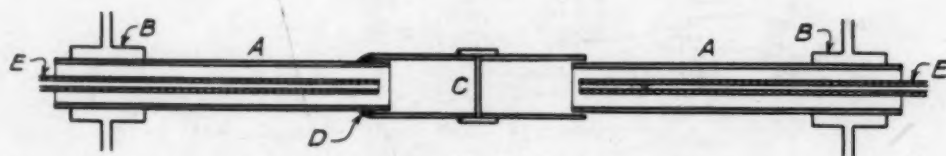


Fig. 3—Arrangement for Final Assembly.

through the stopcock (W). Indeed, the readings can be multiplied theoretically by any amount by partly closing the cock (W).

Greater sensitivity for thick metal sheets at low temperatures and pressures can be obtained by adding a fine capillary after the cock (W). Thus it was possible to measure, in two minutes, diffusion rates that would have taken days using the manometer. However, time must be allowed for the gas flowing through the diffusor to reach equilibrium after any temperature or pressure change is made. The complete experimental arrangement is detailed in Fig. 4.

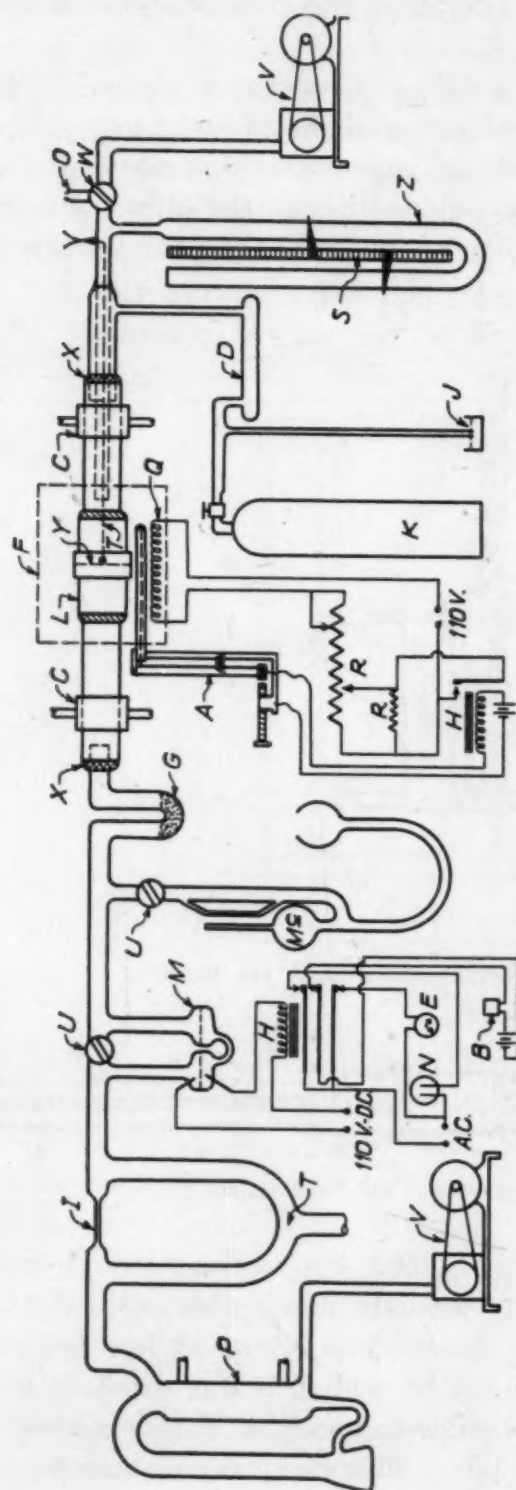


Fig. 4—Apparatus Assembly.

A. Nickel-tungsten thermostat
 B. Electrical buzzer
 C. Water coolers
 D. P_2O_5 drying tube
 E. Electric clock
 F. Furnace
 G. Gold leaf
 H. Electrical relays
 I. Capillary tube

J. Capillary tube in cup of mercury
 K. Tank of gas
 L. Adaptor
 M. Mercury manometer with tungsten contacts
 N. Neon lamp
 O. Opening for excess gas
 P. Mercury vapor pump
 Q. Electric heating coil
 Mc. McLeod Gage

R. Rheostats
 S. Scale
 T. Thermocouple
 U. Stopcocks
 V. Vacuum pumps
 W. Two way stopcock
 X. Glass to adaptor seal
 Y. Disk of metal being tested
 Z. Manometer to measure ingoing pressure

EXPERIMENTAL RESULTS

Results on Nickel and Electrolytic Iron

The reasons for variation in diffusion rates of hydrogen through nickel and electrolytic iron, depending on the history of the sample, have been reported in several early papers by the author (7), (8), (9), (10).

Too much weight should not be given to the numerical data in this earlier work, especially since certain calculations (7) were based

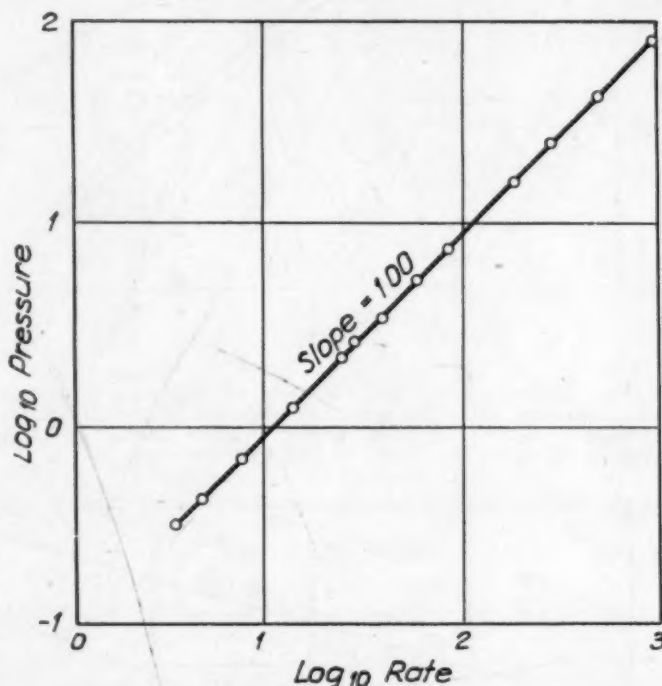


Fig. 5—Relation Between McLeod Gage Reading for Steady Flow and Rates, Determined by a Manometer for a One Millimeter Rise, with Temperature and Volume Constant.

on the data of Borelius and Lindblom (11). The iron used by those investigators in their diffusion work appears to have had small but important amounts of carbon in solid solution.

The new data obtained in the present work are illustrated in Figs. 6 to 16 inclusive.

The number showing the slope of each of the isobars (as in Fig. 9) signifies the value of b obtained from the commonly used

equation, rate $\frac{dm}{dt} = A\epsilon^{\frac{-b}{T}}$, and is sometimes spoken of as the

net work function. As usual b has the dimensions of absolute units of temperature. This can be transformed to calories per gm mol of diffusing gas by multiplying by 2 (approx.).

Figs. 6 and 7 respectively show isobar and isothermal curves

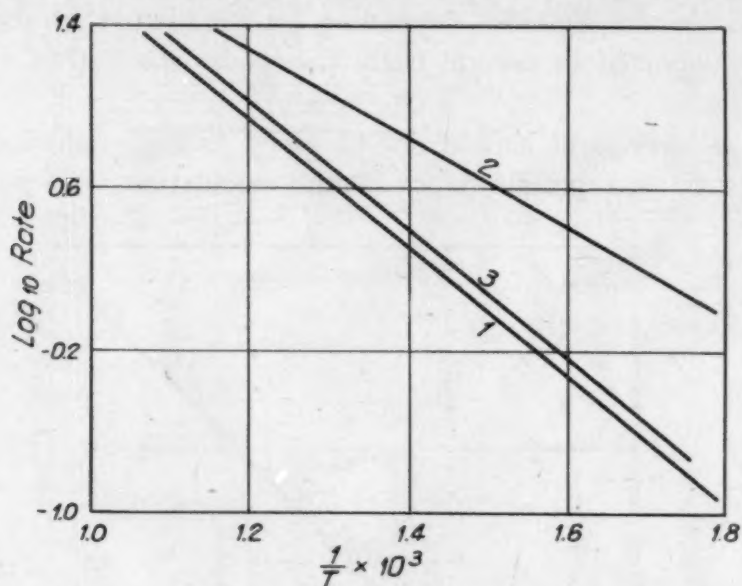


Fig. 6—Isobars for the Diffusion of Hydrogen Through Iron Activated with Nitrogen, (a) Original Rate, (b) After Exposing to N_2 for 144 Hours at 660 Degrees Cent., (c) After Exposing to H_2 for 11 Hours at 710 Degrees Cent.

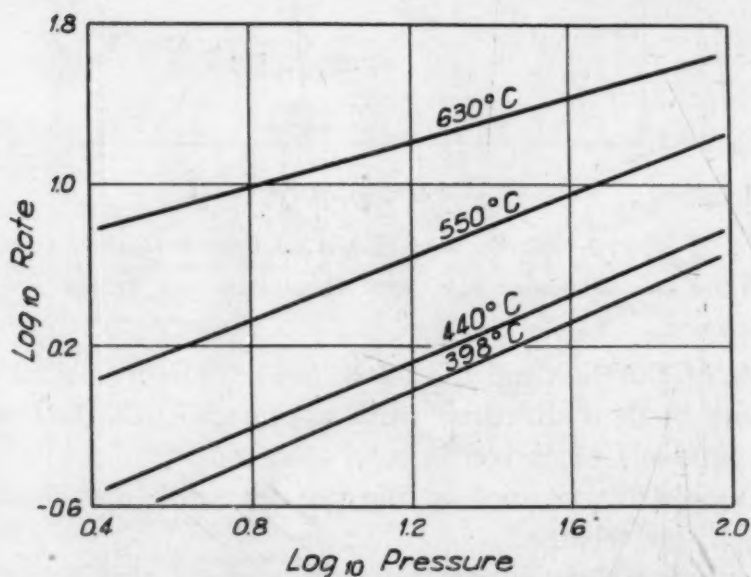


Fig. 7—Isotherms for the Diffusion of Hydrogen Through Iron Activated with Nitrogen.

for hydrogen diffusion through iron alloyed with nickel. The important point shown by these data is the effect of the nitrogen on

the slope of the hydrogen diffusion isotherms (Fig. 7) as well as the effect on the diffusion rate and on the net work function (Fig. 6).

In Fig. 8 are illustrated the hydrogen diffusion conditions obtained with nickel. The isotherms exhibit a gradual change in slope toward 0.50 as the temperature increases. Most of the dif-

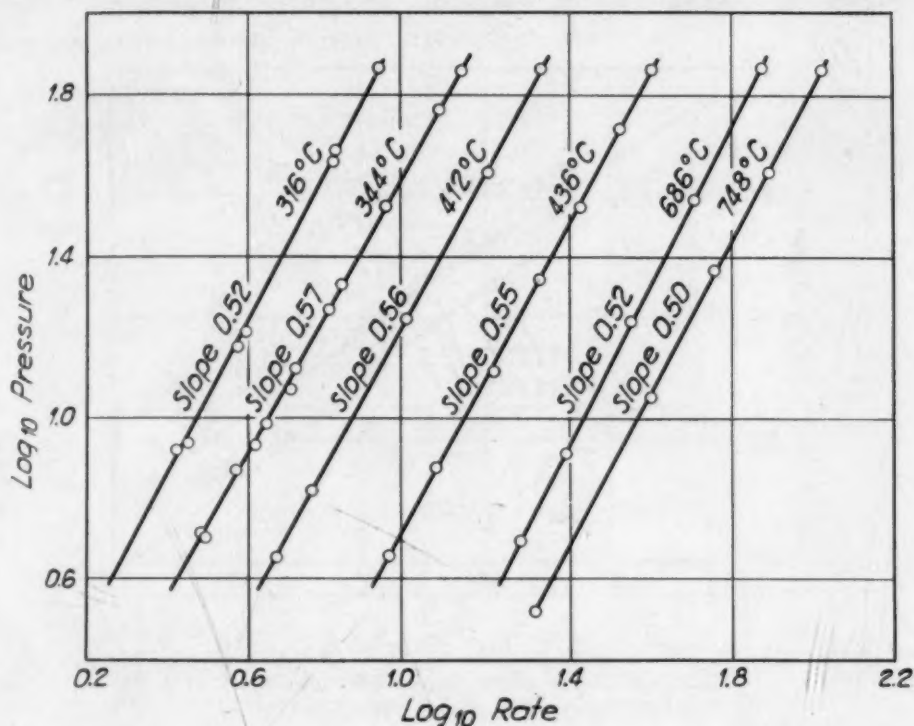


Fig. 8—Isotherms for Diffusion of Hydrogen Through Highly Degassed Nickel.

fusion is accounted for by the formation of Ni_xH . The location of the magnetic inversion of nickel at 365 degrees Cent. is clearly revealed by the change in slope of the isobars (Fig. 9) both by the work of Cranisky and by that of the author. It is of interest to note that an approximate 10-degree rise is necessary to remove the discontinuity in these diffusion isobars.

This marked discontinuity is shown in a 50-pound nickel billet from cooling rate data (Fig. 10), and it corresponds to an equivalent temperature rise of about 10 degrees Cent. In the work of Hedvall (12) on the variation with temperature of the rate of the reaction $NO_2 \rightarrow NO + \frac{1}{2}O_2$ in the presence of a nickel catalyst (Fig. 11), the same discontinuity appears at the 360 degrees Cent. temperature. Again a change of 10 degrees Cent. is required to remove this discontinuity.

In Figs. 12 and 13 may be observed the linear character of the diffusion isobars for electrolytic iron between 350 and 730; 770 and 840; 840 and 900; 900 and 954; and 954 and 990 degrees Cent. The change in slope is dependent on the sample used but is independent of direction of flow of hydrogen.

The region 730 to 770 degrees Cent. (Fig. 14) checks well with

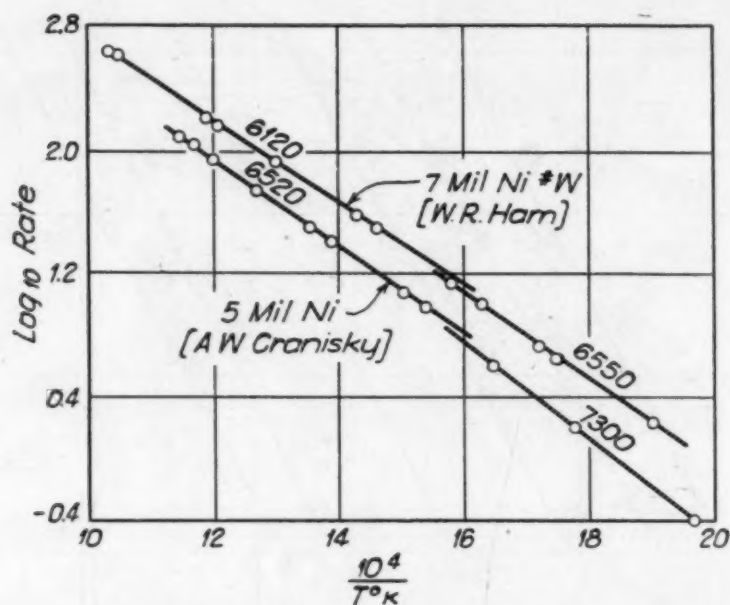


Fig. 9—Diffusion of Hydrogen Through Nickel at 1 Atmosphere. Curve No. 1—7 Mil Nickel, Curve No. 2—5 Mil Nickel.

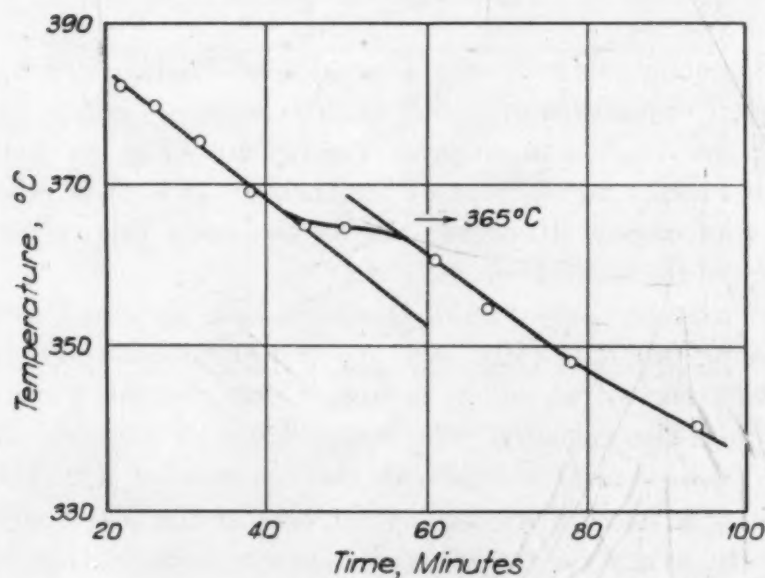


Fig. 10—Cooling Curve of a Nickel Billet.

the demagnetization curve of Benedicks (13), and the change at 900 degrees Cent. (Fig. 12) is evidently associated with the allotropic transformation. The slight change at 840 degrees Cent. (Fig. 12) also correlates with the dilation work of Benedicks (13) for electrolytic iron. The large break at about 200 to 350 degrees Cent. (Fig. 13) has considerable hysteresis and may be associated with the well known maximum in the tensile strength.

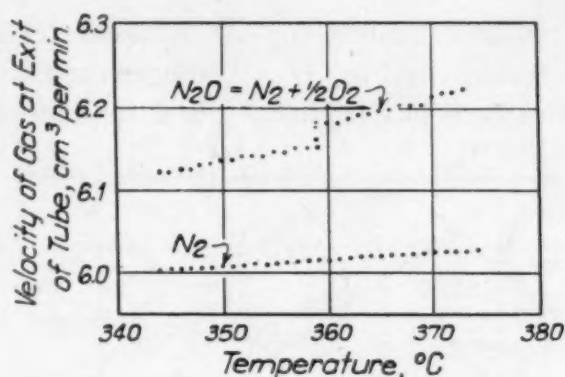


Fig. 11—Catalytic Activity at the Magnetic Transition Point.

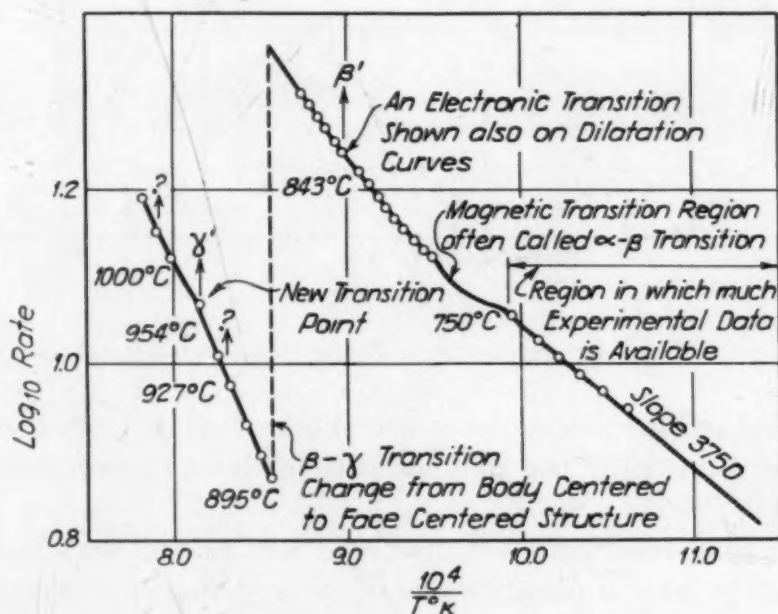


Fig. 12—Diffusion of Hydrogen Through Electrolytic Iron.

The isotherms for the material have a slope of 0.50 within experimental error (Fig. 15). This slope is maintained above or below and in the region of any transition. Thus it may be inferred that

the iron is free from carbon, and degassed except for hydrogen. Furthermore, the position of the transition is unaffected by hydrogen.

In the last Fig. (16) are assembled data on an iron-nickel alloy. The temperature depression of the allotropic inversion is well shown, but this inversion is unaffected by hydrogen concentration.

Results on Relatively Pure Iron

The modified arrangement for the diffusion tests on this section of the work is shown in Fig. 17. Duplicate tests were run simultaneously. Some care has been exercised in temperature measure-

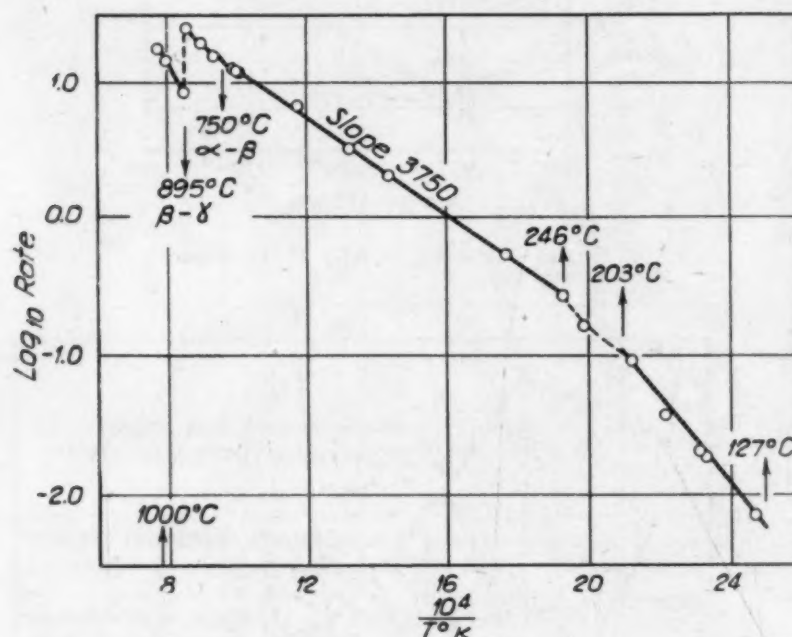


Fig. 13—General Diffusion of Hydrogen Through Electrolytic Iron.

ments and the thermocouples were calibrated while almost in contact with the diffusor by use of a pure silver bead observed through a telescope.

The chromel-alumel thermocouple was placed near to the diffusor on the normal pressure side of the system and then as the temperature approached the melting point of silver, the silver bead, held in an iron sheath, was brought up to the other face of the diffusor by means of an electromagnet. This iron holder protects the diaphragm from any silver which may be vaporized on the low pressure side.

Thus by observing the thermal e.m.f. at the instant of melting of the silver accurate check calibration is possible.

Preparation of samples for diffusion without contamination necessitated much study. The iron for the tests in this section was ob-

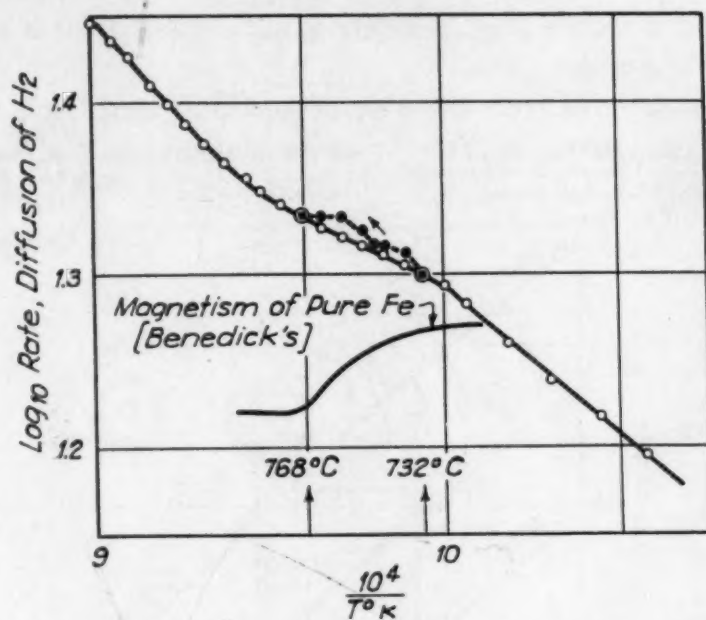


Fig. 14—Iso-bar for Diffusion of Hydrogen Through 15 Mil Iron.

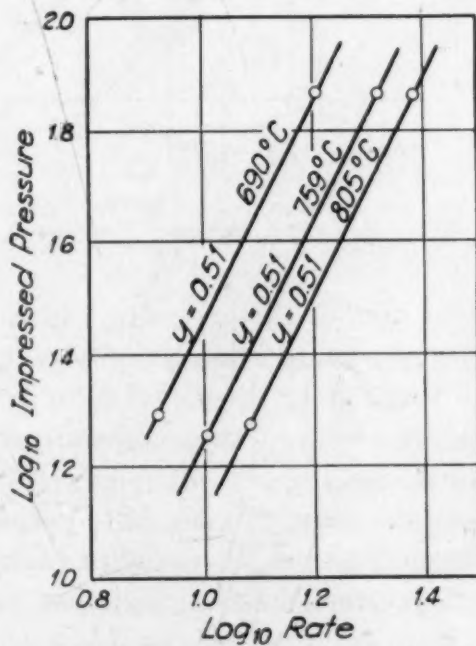


Fig. 15—Isotherms for Hydrogen Through 15 Mil Iron.

tained from the Westinghouse Company (kindly supplied by Dr. T. D. Yensen) and is referred to as Yensen iron in this paper.

The developed technique for assembling a diffusing sheet for this work is as follows:

1. A piece of nickel tube, 1-inch outside and $\frac{3}{4}$ -inch inside diameter and 2 inches long, is cleaned and degassed for a short time at about 1000 degrees Cent.
2. A sample of iron about 0.120 to 0.150 inch thick at start is turned to a disk that is a press fit in the above nickel tube.

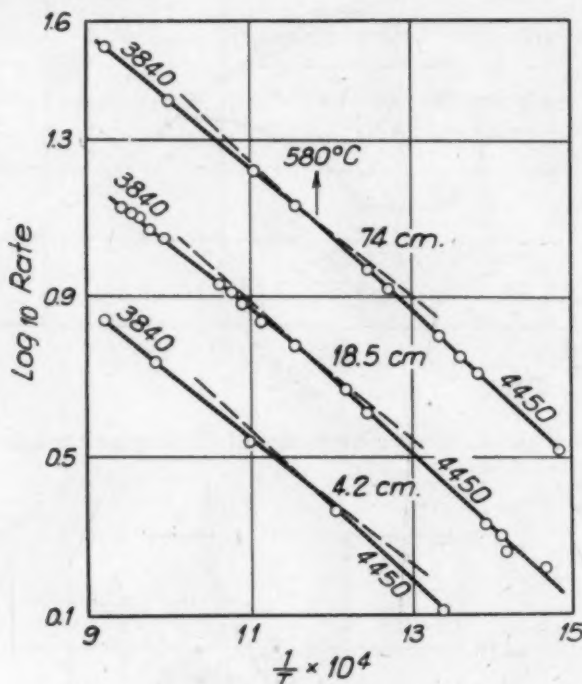


Fig. 16—Diffusion Isobars for Iron Alloyed with Nickel at Various Impressed Pressures.

3. The center $\frac{1}{2}$ area of this iron disk is turned to a thickness of 0.040 to 0.050 inch by cutting symmetrically on both sides.*

4. The disk is forced into the nickel tube by means of a hard steel cylinder and large vise or press, a pressure of about 2 tons generally being used.

5. Nickel tubes (the same that are later permanently installed) are pressed into each end of the tube section containing the sample and when in a vertical position, small nickel tubes of $\frac{1}{4}$ -inch external

*Note: Operation 3 is sometimes left until the center assembly has been made, but no different results are observed and the procedure as written is more convenient.

diameter are run in either end and a rather strong current of hydrogen blown against each of the machined faces of the sample.

Around the upper edge of the sample and touching the nickel holder a single turn of No. 24 gold wire has been placed, before the upper tube has been pressed on. With the hydrogen flowing so

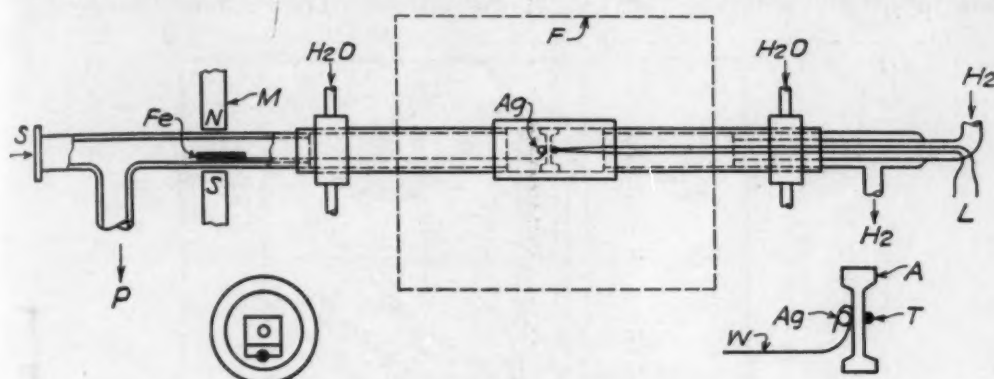


Fig. 17—Method for Calibrating Thermocouples.

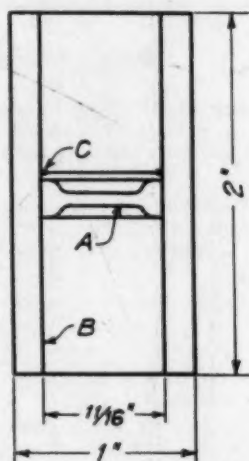


Fig. 18—Later Method of Assembling a Diffusing Disk.

as to furnish a good sized flame two or three inches high at both ends, a gas-oxygen torch is played around the center of the nickel tube containing the specimen, until the melting point of gold is reached. This takes 2 minutes. The gold, of course, is drawn by capillarity into the pressed fit making a very perfect joint. The finished diffuser in its holder is illustrated in Fig. 18.

The parts are then disassembled and the iron specimen gold welded in its nickel holder remachined all over. Most of the diffusion will take place through the thin central section, and the time

required for the gold to cause any trouble there should be very great, the rate of diffusion of gold into iron being slow. Gold, incidentally, will not diffuse any gas so far as is known and seems to be the truly noble metal in this respect.

The process to this point never gave any trouble from the start, but in finally welding the longer end tubes of nickel to the central

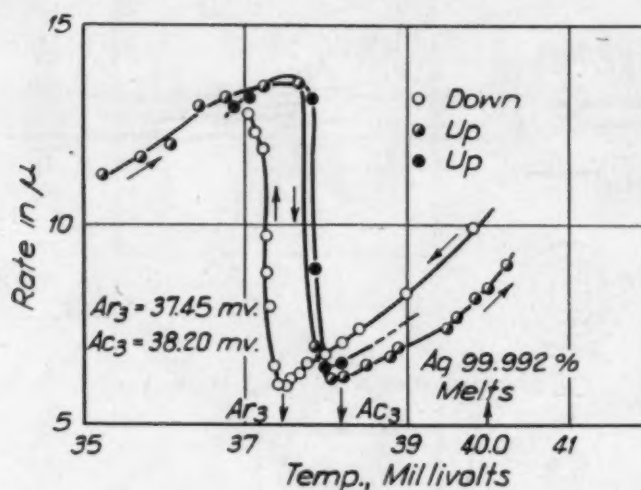


Fig. 19—Direct Plot (Rate Versus Millivolts of Thermocouple) of a Sample of Yensen Iron When First Taken Several Times Through the Body-Centered—Face-Centered Transition.

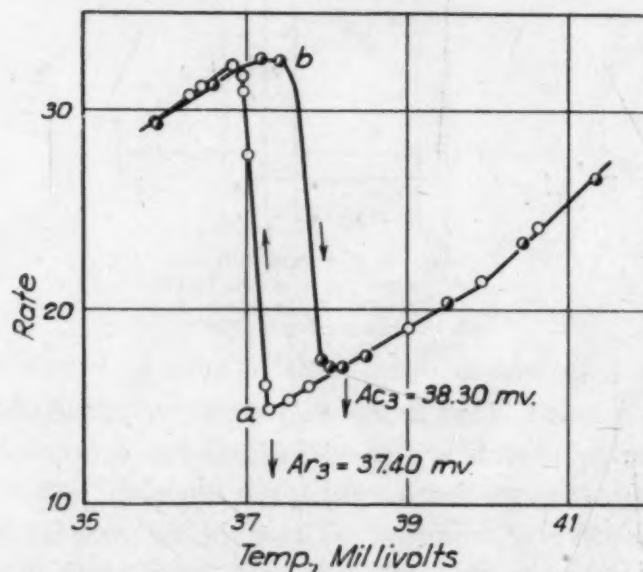


Fig. 20—Same as Sample in Plot I, After Heating at 1000 Degrees Cent. for 1 Hour.

tube, particularly if an atomic hydrogen torch were used in the process, nickel invariably vaporized on the inside and particularly

on both sides of the diffusor and ruined it. It is easy enough to tell when this has occurred for the gamma transition appears lower and lower as hydrogen runs are taken and as the vaporized nickel (or copper) diffuses into the interior of the diffusing sheet.

However, one can completely protect the iron diffusing sheet by pressing over either face a thin sheet of nickel or iron (generally $\frac{1}{2}$

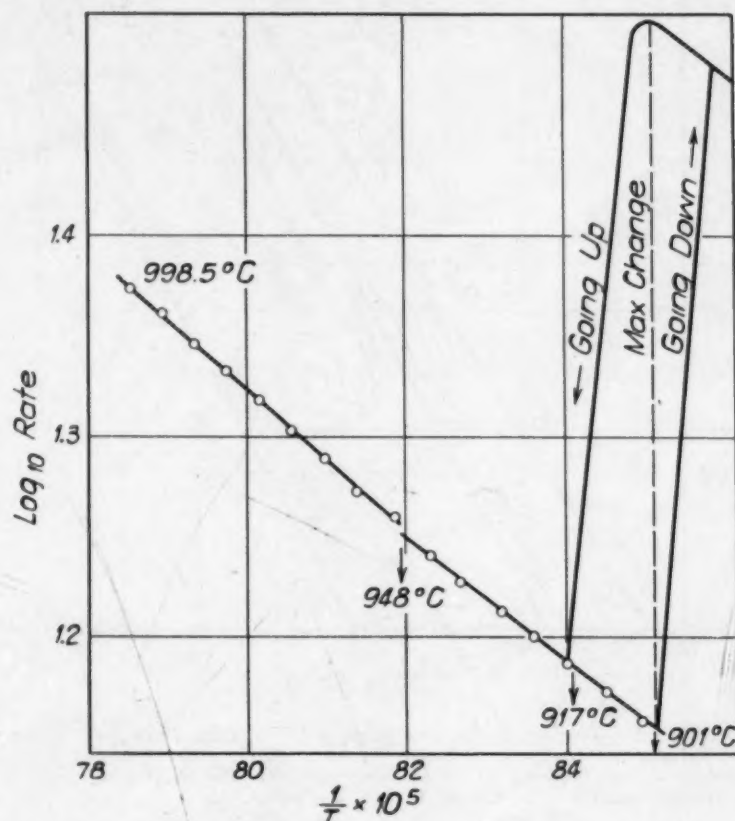


Fig. 21—Same Data as of Plot II, Represented on the Log Rate Versus $1/T$ Basis.

mil nickel was used) performing the necessary welding operations, always with hydrogen on the inside, then reaching in either end of the assembly with a suitable hook and removing the protecting sheets.

At the time of writing, two similar diffusing sheets of iron have maintained their gamma transition point unchanged within experimental error for six weeks and hence apparently neither gold nor nickel has yet reached the main diffusing section in sufficient amount to affect hydrogen diffusion rates. During much of the time, however, the temperature has been low (around 200 to 400 degrees Cent.). Of course the ideal arrangement would be to have most of the heated section made of the material whose diffusion char-

acteristics one wishes to investigate, but that seems hardly possible in many cases on account of the form in which the samples may be obtained.

A fairly complete set of graphs showing the hydrogen diffusion characteristics of Yensen iron now follows in Figs. 19 to 26.

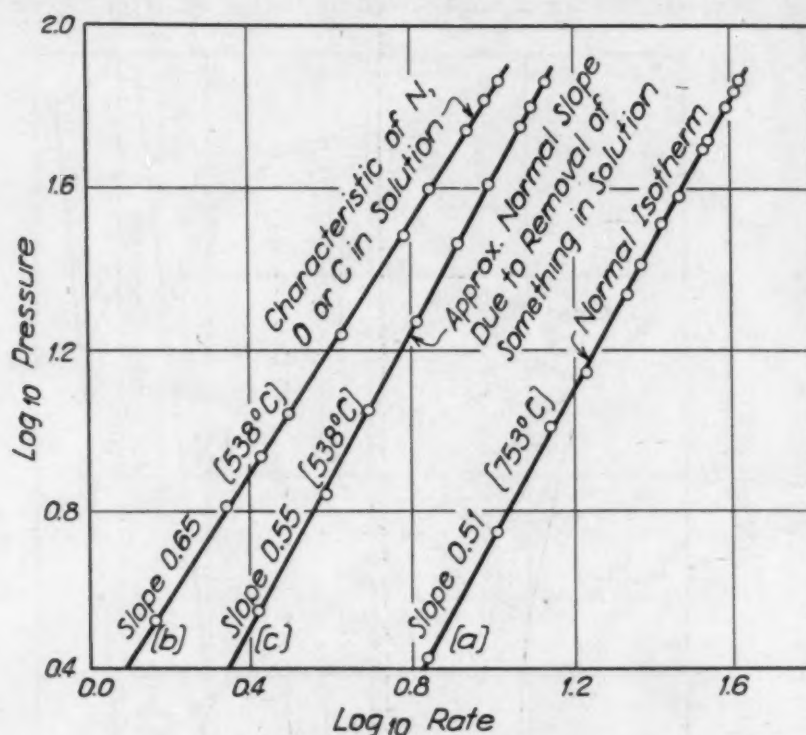


Fig. 22—Isotherms for the Sample of Yensen Iron (a) Taken in the Middle of the Curie Region, (b) at a Fairly Low Temperature, (c) Results After Holding at 1000 Degrees Cent. for 2 Hours, With Dry Hydrogen and then Reducing to 538 Degrees Cent.

The first observations, taken before degassing, on the relation between temperature and diffusion rate on heating and cooling are shown in Fig. 19. After holding at 1000 degrees Cent. for about 1 hour and during calibration of the thermocouple, helium was substituted for hydrogen and the rate of degassing observed down to 800 degrees Cent. at which temperature the McLeod gage would no longer indicate any pressure. Repeat isobars now show (Fig. 20) about 16 degrees Cent. spread in the Ar_3 and Ac_3 with a mean value of 909 degrees Cent. It should be emphasized that the location of these discontinuities is independent of rate of heating or cooling.

Thus the temperature was held over night near (b) and for several hours at (a) without transformation taking place (Fig. 20). The behavior in this region is to receive particular attention by the

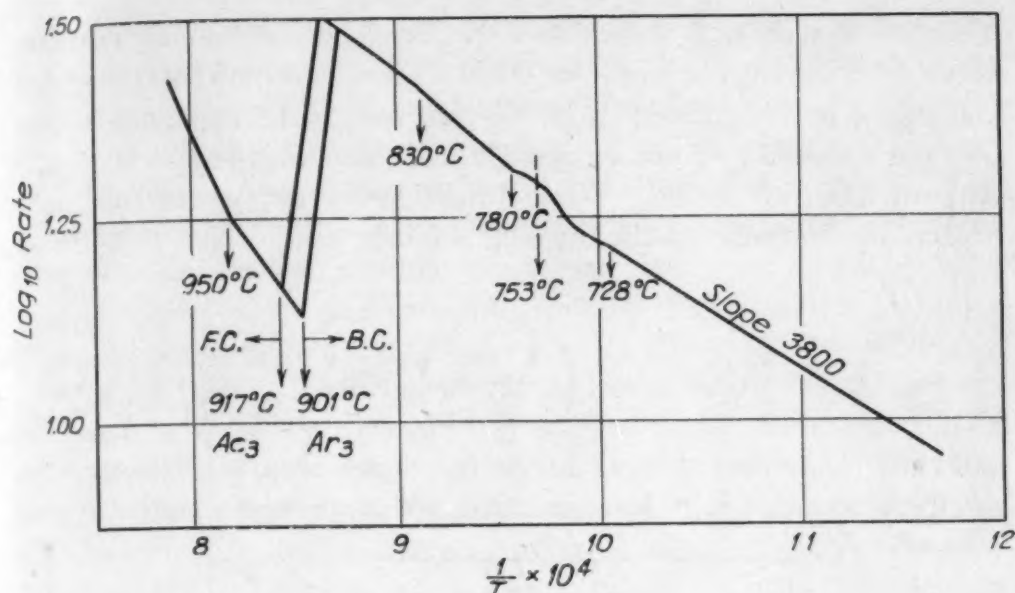


Fig. 23—General Diffusion Plot for Yensen Iron.

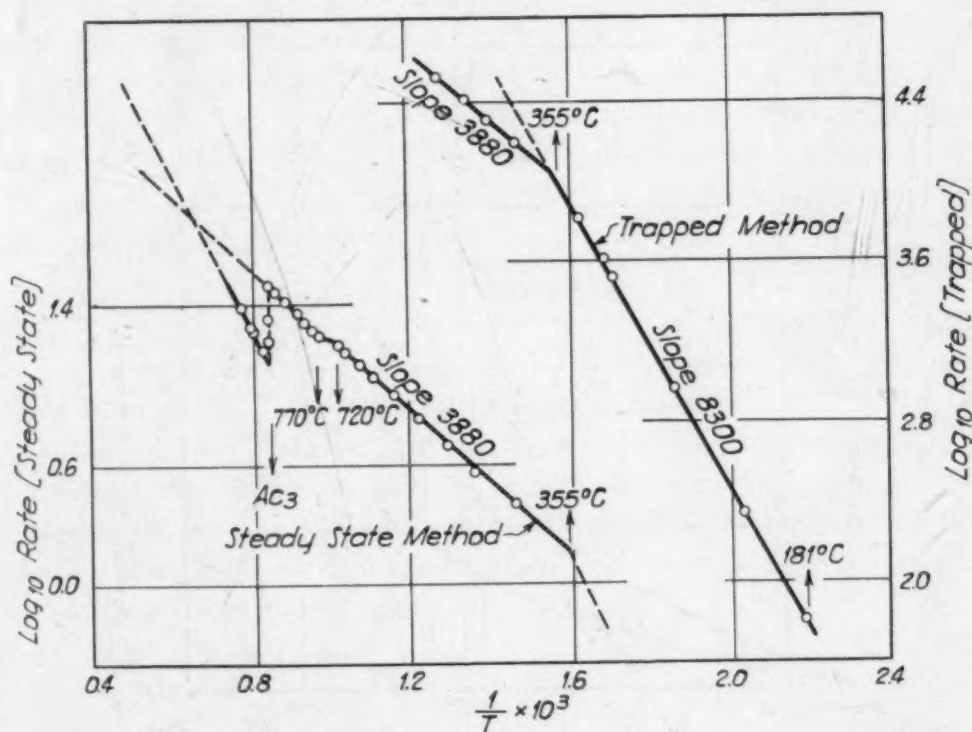


Fig. 24—General Diffusion Plot for Yensen Iron Over a More Extended Region.

author in further work. Plotted in the form of an isobar the data considered show a small break, previously noted, at 950 degrees Cent. (Fig. 21).

The effects of impurities on the slope of the isothermals for

Yensen's iron is well shown in Fig. 22. The slope of an isotherm taken at 538 degrees Cent. is 0.65. This is somewhat surprising and might be interpreted as an isolated case to be explained by the idea put forward by Smithells and Ransley (6) with regard to similar data of Borelius (11). These investigators apply the Langmuir adsorption formula to the ingoing surface and derive a diffusion formula,

$$R = A \left(\frac{1 - ap}{ap} \right) p^{\frac{-b}{T}}$$

and thus imply that the gas inside the metal always exists there as single atoms or ions. However, since the slope of an isotherm may

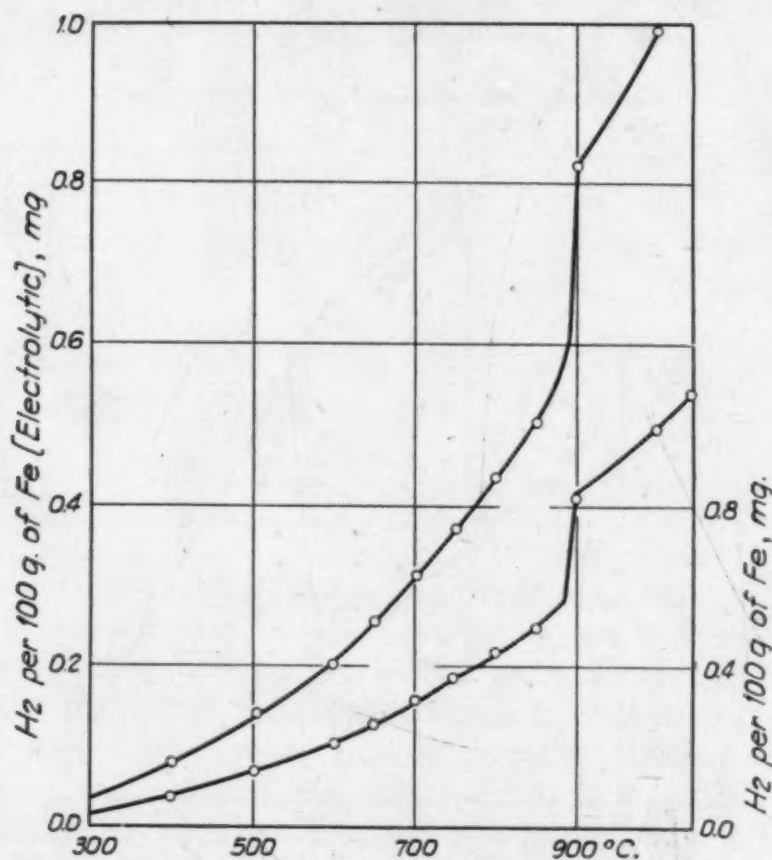


Fig. 25—Sievert's Data for Solubility of Hydrogen in Iron.

easily be modified and controlled by adding or removing either carbon or nitrogen from solution, and since the plot is still linear (see Fig. 22), the argument with regard to applying the Langmuir adsorption factor to a diffusion formula is not convincing. Thus 2 hours at

1000 degrees Cent. in hydrogen changes the slope of the isotherm at 538 degrees Cent. from 0.65 to 0.55 (Fig. 22). Four more hours of such treatment brought this isotherm slope to 0.50.

It is difficult to explain this behavior by introducing the Langmuir adsorption factor to correct the usual diffusion formula. Fig. 23 represents the diffusion rate over a temperature range extending from the highest temperature the author has used (1000 degrees Cent.) to the lowest temperature generally found in the literature (350 degrees Cent.).

Fig. 24 shows a plot in which the temperature range has been extended on the lower side to 180 degrees Cent. The slope of the diffusion isobar from the Curie region down to about 350 degrees Cent. is 3880 degrees which approximates to the value of 3800 degrees recorded in the literature by other observers (6). A profound change, however, is observed below 350 degrees Cent. and down to 180 degrees Cent. where the slope is 8300 degrees. In this region, however, the diffusion data were taken before any extended heat treatment in hydrogen at 1000 degrees Cent.

Sievert's (14) data for solubility of hydrogen in iron (Fig. 25) permits a rough calculation of carbon concentration which may have produced the slope of 0.64 in the 538 degrees Cent. isotherm (Fig. 22). Since 100 grams of iron holds 0.15 milligram of hydrogen in solution at this temperature

$$\text{Per Cent Ratio} \frac{\text{H atoms}}{\text{Fe atoms}} = \frac{0.00015 \times 55.8 \times 100}{100} = 0.0084 \text{ Per Cent}$$

Assuming that the cause of excess slope above 0.5 is due to carbon in solution, that each carbon atom is paired with two hydrogen atoms, and that diffusion is of a double type in which part of the hydrogen ($100 - X$) in solution is in single ions, and the remainder (X) in double ions, the mass action exponent observed may be considered as a resultant of:

$$(X) \cdot (1.00) + (100 - X) \cdot (0.5) = 0.64$$

Here $X = 28$ and $100 - X = 72$

$$\text{Per Cent C in solution} = \frac{1}{2} \cdot \frac{28}{100} (0.0084) = 0.001 \text{ per cent (atomic)}$$

$$= 0.001 \times \frac{14}{56} = 0.0002 \text{ per cent (by weight)}$$

A similar effect should be caused by nitrogen.

No attempt has been made to develop this form of analysis and all that can be stated with certainty is that heat treatment of 0.040 inch sheet iron in dry hydrogen at over 1000 degrees Cent. for 2

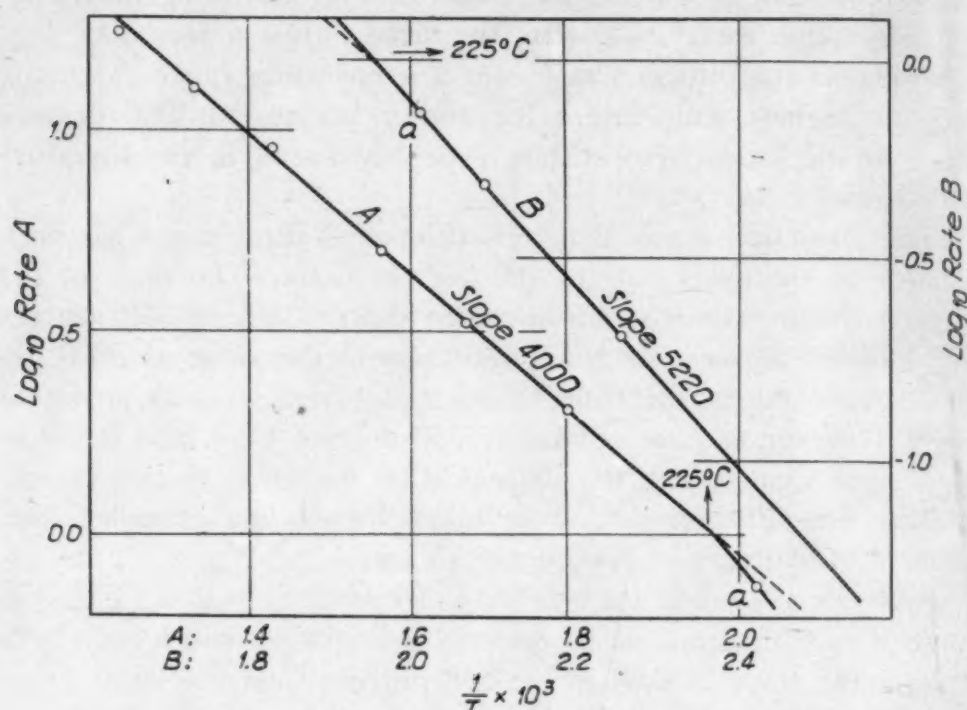


Fig. 26—Isobar for Yensen Iron Shows a Low Temperature Diffusion Break After the (Total) 5 Hours Heat Treatment.

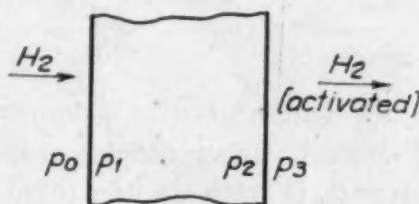


Fig. 27

hours and in dry nitrogen for 3 hours has removed something that originally caused the slope of this low temperature isotherm to be far above normal.

Fig. 26 shows the low temperature diffusion break after the 5 hours heat treatment of the iron. A marked lowering of this transition from that originally shown (Fig. 24) is at once evident. Furthermore, the change in slope is much less. Carbon removal has the same general effect on the peak, observed in correlating tensile strength with temperature.

THEORY OF HYDROGEN DIFFUSION IN NICKEL AND IRON

If we consider a homogeneous metallic sheet through which hydrogen is flowing having the pressures p_0, p_1, p_2, p_3 as shown in Fig. 27 and imagine a pump sufficiently fast to always make $p_3 = 0$

$$\text{I. } \frac{dm}{dt} = p_2 \left(\frac{m}{2\pi KT} \right)^{1/2} e^{-\int_0^T \frac{\Phi dT}{KT^2}}$$

follows at once from Kinetic Theory, where Φ is the total work performed by the diffusing particle of mass, m , in passing through the back surface and is in general a function of T , K the Boltzman Constant, and T the temperature in degrees Kelvin.

Φ may be considered as made up (1) of Δw the difference between the heat of formation of the inside aggregation of metal and hydrogen and the heat of formation of outside normal molecular hydrogen.

(2) Of a surface work function (b) that is the difference in energy between the normal ingoing hydrogen and the escaping excited hydrogen.

Hence $\Phi = b - \Delta w$ and its variations with temperature will depend on the number of degrees of freedom of the diffusing material inside and outside the surface; furthermore, a linear variation of b and Δw with temperature over the range used is assumed to be sufficiently exact in the range of temperatures used.

Or $\Phi = b_0 - \Delta w_0 + n KT$ where n is not necessarily a whole number, also assuming the degrees of freedom on the inside to be less than on the outside to account for the plus sign before the $n KT$.

Integrating we have,

$$\text{II. } \frac{dm}{dt} = p_2 \left(\frac{m}{2\pi K} \right)^{1/2} T^{n-1/2} e^{\frac{-b_0 + \Delta w_0}{KT}}$$

Since it is simpler to use absolute temperatures in representing data it is convenient to introduce new work functions that have the dimension of temperatures; i.e.,

¹See Loeb's Kinetic Theory of Gases.

$$\text{III.} \quad \frac{dm}{dt} = p_2 \left(\frac{m}{2\pi K} \right)^{1/2} T^2 \epsilon \frac{-B_0 - \Delta W_0}{T}$$

Z replacing $(n - 1/2)$ and capital letters now used for the work functions.

Experimentally, the rate varies inversely as the thickness of a sheet other things being constant, or $p_2 = \frac{p_1 a}{X}$; this amounts to Fick's Linear Diffusion Formula

$$\text{IV.} \quad \frac{dm}{dt} = a \frac{dp}{dx} \text{ (often written)} \quad \frac{dm}{dt} = D \frac{dc}{dx}$$

The function that D (or a) is of T has been determined by Langmuir and Dushman and others. The relation between a and D is found at the end of the theoretical discussion.

Substituting IV in III, we have,

$$\text{V.} \quad \frac{dm}{dt} = \frac{p_1 a}{X} \left(\frac{m}{2\pi K} \right)^{1/2} T^2 \epsilon \frac{-B_0 - \Delta W_0}{T}$$

We may interpret p_1 in terms of outside equilibrium pressure of molecular hydrogen; that is, apply a mass action formula. This would in general appear to be* $p_1 = A p_o^y$ where p_o is the external equilibrium pressure of molecular hydrogen and p_1 is the internal mean pressure of the hydrogen in whatever form of aggregation it may be. Then by further substitution, it follows that,

$$\text{VI.} \quad \frac{dm}{dt} = \frac{A p_o^y a}{X} \left(\frac{m}{2\pi K} \right)^{1/2} T^2 \epsilon \frac{-B_0 - \Delta W_0}{T}$$

However, $A = A_0 \epsilon \frac{-\Delta W_0}{T}$ where ΔW_0 is the heat of activation of molecular hydrogen going into the first surface. Moreover

*Perhaps the experimental results on the form of diffusion isotherms would be considered the best proof of this relation.

$a = a_0 \epsilon^{\frac{-C}{T}}$ where C is the heat of activation (internal) of the diffusing hydrogen necessary to cause it to change from one lattice position to the next similar position that it is to occupy.

Substituting the above values for A and a in VI gives

$$\frac{dm}{dt} = \frac{A_0 a_0 p_o^{\gamma_0}}{X} \left(\frac{m}{2\pi K} \right)^{\frac{1}{2}} T^{\frac{1}{2}} \epsilon^{\frac{-B_0 - \Delta W_0 + \Delta W_0 - C}{T}}$$

Or,

$$\text{VII.} \quad \frac{dm}{dt} = \frac{A_0 a_0 p_o^{\gamma_0}}{X} \left(\frac{m}{2\pi K} \right)^{\frac{1}{2}} T^{\frac{1}{2}} \epsilon^{\frac{-B_0 - C}{T}}$$

The ΔW has disappeared from the equation and B_0 appeared since the *outgoing* hydrogen is excited, i.e., B_0 is really the difference in energy content expressed in degrees absolute of the ingoing and outgoing hydrogen.

There are two more points to be discussed before the equation for diffusion is in final form.

(a) p_o is not the pressure of the impressed hydrogen, but the *equilibrium* pressure on the outside that would give the pressure p_1 just inside the first surface. We are not discussing equilibrium but rather steady flow, and in this case P_o the actually impressed pressure is slightly larger than p_o ; however, computations show that the difference is too small to measure so for this discussion $P_o = p_o$ will be written.

(b) The exit pressure (p_3) is never zero. A correction for this is easily made by writing the diffusion equation for back flow using p_3 as the impressed pressure and subtracting the resulting flow from that already computed.

Taking (a) and (b) into account one obtains as a final result,

$$\text{VIII.} \quad \frac{dm}{dt} = A_0 a_0 \left(\frac{P_o^{\gamma_0} - p_3^{\gamma_3}}{X} \right) \left(\frac{m}{2\pi K} \right)^{\frac{1}{2}} T^{\frac{1}{2}} \epsilon^{\frac{-B_0 - C}{T}}$$

an equation that except for one rather important item (i.e., the exponent of the p 's) is about the same that has been employed by most observers.

Concerning the variable exponent y used in the theory it appears that the diffusion of hydrogen through a pure metal (or a solution of hydrogen in such metal) is effectively represented by $\frac{1}{2} \text{H}_2 \rightleftharpoons \overset{+}{\text{H}} - \epsilon$, in other words, the mass action exponent in such diffusion is $\frac{1}{2}$ and experimental results bear this out. There are, however, important exceptions. If the metal such as iron already has carbon or nitrogen in solution, much of the hydrogen put in solution, when said carbon or nitrogen is "frozen" in place, seems to aggregate at the points where the nitrogen or carbon exists and elsewhere to live as single ions. The picture is not that the hydrogen moves away as aggregates from the position of the carbon or nitrogen but rather that the field in the region of the nitrogen or carbon is such that two (or more) hydrogen ions are temporarily stable there.

A condition of double diffusions may raise the mass action exponent toward unity by an amount depending upon the relative concentration of certain impurities in the metal with respect to hydrogen present.

Since isotherms taken after iron (or palladium) is charged with nitrogen or carbon are always *straight* when plotted $\log \text{Rate}$ a $\log \text{Pressure}$ with T constant even although the slope is much above .5 in value, the correct expression in the general formula seems to be p^y_0 and not $p^{1/2}_0$, although it must be admitted that the latter form seems to obtain when diffusing hydrogen through metals relatively pure and free from other gases and carbon.

The constants of the general formula are ordinarily grouped and it is written,

$$\frac{dm}{dt} = A P^y_0 T^z e^{\frac{-b}{T}}$$

Very often the exponent Z is assumed to be about zero and then

$$\text{IX.} \quad \frac{dm}{dt} = A P^y_0 e^{-b/T}$$

and if treating simple diffusion in a relatively pure metal,

$$\text{X.} \quad \frac{dm}{dt} = A P^{1/2}_0 E^{-b/T}$$

This last is the commonly used diffusion equation and fits most experimental data of diffusion of gases through metals over a temperature range that is surprisingly wide in many cases.

In metals such as nickel and iron in which rearrangement of electrons in the individual atoms takes place more or less abruptly as the temperature is changed, the formula is applicable only in such temperature ranges where no electronic transition occurs.

A comparison of that internal section of the general diffusion formulae from the concentration standpoint (Langmuir and Dushman) with similar equations developed from pressure standpoint follows.

Fick's Linear Diffusion Formula applied to internal diffusions in a metal lattice.

Pressure

$$\frac{dm}{dt} \frac{1}{cm^2} = a \frac{dp}{dx}$$

$$p = C R T$$

$$\frac{dp}{dx} = R \frac{dC}{dx}$$

Or $a = \frac{D}{R}$ if p is expressed
in dynes/cm²

$$a = \frac{C}{Nh} \delta^2 e^{\frac{-c}{T}}$$

$$a = a_0 e^{-c/T}$$

$$a_0 = \frac{c \delta^2}{Nh}$$

Concentration

$$\frac{dm}{dt} \frac{1}{cm^2} = D \cdot \frac{dC}{dx}$$

Where C is the weight in grams of diffusing particles per cu. cm.

$$D = \frac{2}{Nh} \cdot \delta^2 e^{\frac{2}{RT}}$$

If $\frac{2}{R} = c$

$$D = \frac{Rc}{Nh} \cdot \delta^2 e^{\frac{-c}{T}}$$

$$D = \frac{K}{h} \cdot c \cdot \delta^2 e^{-c/T}$$

$$D = D_0 e^{-c/T}$$

$$D_0 = \frac{K c \delta^2}{h} = \frac{Rc}{Nh} \cdot \delta^2$$

Units are so chosen that D has dimensions of $L^2 T^{-1}$ i.e.,

$$D = \frac{M L}{T L^2 \frac{M}{L^3}} = L^2 T^{-1} \text{ or concentration is defined in terms}$$

of grams per cubic centimeter. Either a_0 or D_0 may be thought of as the internal diffusion coefficient.

Meaning of Symbols Used

- m = mass in grams
- p = pressure in dynes/cm²
- C = Concentration in weight in gm. per cu. cm.
- D = Diffusion coefficient on a concentration basis
- a = Diffusion coefficient on a pressure basis
- ϵ = Heat of Diffusion
- c = Diffusion work function in degrees
- N = Number of atoms in a Gram-Atomic Weight
- h = Planck's constant
- R = Gas Constant
- K = Boltzman Constant
- δ = Interatomic distance
- T = Absolute Temperature

SUMMARY

A diffusion formula based on classical kinetic theory and thermodynamics explains within experimental error the diffusion of hydrogen through iron and nickel provided the metals remain homogeneous, that is provided no transition points are encountered.

In the case of these two metals marked changes in diffusion of hydrogen occur at the Curie regions, though the formula still holds, above and below these regions.

Particularly significant is the almost equal temperature change required to eliminate discontinuities at the Curie point of nickel in such diverse relations as in (1) hydrogen diffusion through nickel, (2) cooling of pure nickel, (3) reactions brought about by nickel catalyst. The conclusion can hardly be avoided that the nature of the bonding between the various nickel atoms in its simple lattice is

essentially the same as that between these nickel atoms and the hydrogen or oxygen atoms diffusing within the lattice.

Any alloying of the above mentioned metals with nitrogen (and probably with anything else) changes their hydrogen diffusion characteristics. Nitrogen increases diffusion rates and lowers the work function. The mass action exponent may increase from 0.5 for the pure metals or alloys, toward unity in case of iron or alloys of iron charged with nitrogen. Carbon in solution seems to have a similar effect on increasing the mass action exponent, that is the slope of a hydrogen diffusion isotherm. The use of the Langmuir adsorption isotherm to explain curved isotherms showing the rate of diffusion of hydrogen through iron when such rate is plotted against the square root of impressed pressure is surely incorrect, since such curvature may be controlled by varying the amount of certain other elements in solution in the iron.

The diffusion of hydrogen enables one to locate transition points with a degree of accuracy, limited only by heat control and temperature measuring devices, and for such concentrations as are ordinarily used, the location of the points is independent of the presence of hydrogen.

From the transition points of electrolytic iron as shown by hydrogen diffusion, one can predict all the points at which radical physical changes of any nature occur, such as changes in elongation, tensile strength, magnetic permeability, conductivity, and crystal structure.

That rather pure iron suffers marked transition in the region between 200 and 350 degrees Cent. seems clear, and the variation of the temperature of such transition with change in concentration of carbon is very similar to the variation of the maximum in the tensile strength. As such iron (referred to in the text as Yensen iron) is more completely decarburized, the change in net work function at the above mentioned low temperature break becomes less marked, however during the removal of these last traces of carbon there is little evidence that the Ac_3 and Ar_3 points tend to approach each other.

In the form of an acknowledgment at the end of this paper note is made that much of the experimental data was taken by J. D. Sauter, Graduate Assistant in the Physics Department at The Pennsylvania State College. Many of the improvements in technique were due to Mr. Sauter's efforts and most of the diagrams and graphs

were drawn by him. Dr. C. R. Austin, associate professor of metallurgy in the School of Mineral Industries of The Pennsylvania State College, has been of great assistance in editing the paper. Valuable suggestions have been offered from time to time by Drs. W. P. Davey, J. H. Simons and N. W. Taylor, all of the institution mentioned, and many others at other places have contributed in some way.

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DISCUSSION

Written Discussion: By C. Wells, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh.

It is interesting to find in this paper diffusion data being used for the determination of phase and electronic changes in metals and alloys. While the method can be used to determine the A_2 temperature and the Curie point in iron, as indicated by the author, it is unlikely to find a general application in such fields, because the A_2 temperature in iron can be determined conveniently and more precisely by the dilatometric method,¹ and the electronic changes can be more adequately studied by the thermomagnetic method. That thermomagnetic curves are more instructive than diffusion isobars for indicating more completely the temperature range of the Curie electronic disturbance in iron is apparent from a comparison of the thermomagnetic curve of Honda² (Fig. A, top curve) with the isobar of Fig. 14. It is seen that the isobar, unlike the magnetic curve, shows no evidence of an electronic change between room temperature and 760 degrees Cent. (1400 degrees Fahr.). The reason for the

¹C. Wells, R. A. Ackley and R. F. Mehl, *TRANSACTIONS*, American Society for Metals, Vol. 24, 1936, p. 46.

²K. Honda, "Magnetic Properties of Matter," p. 81. Syokwabo and Company, Tokyo, Japan, 1928.

better agreement between the thermomagnetic curve and the isobar of Fig. 14 is that in Benedick's work a much less H (magnetizing force) value was used than was the case when Honda's experiments were made, with the result that Benedick's iron was less saturated than that of Honda. The present ferromagnetic theory³ demands, and experimental evidence from many sources shows,

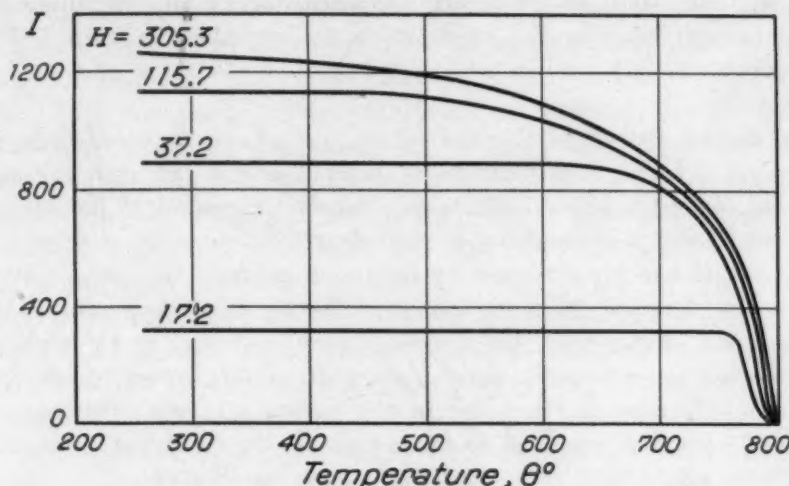


Fig. A—Taken from Honda's Book, Page 81.

that the flux in magnetically saturated ferromagnetic materials decreases with temperature from 0° (absolute) to the Curie point. It is quite evident from this and the results of Professor Ham that there is a considerable temperature range in which the results of diffusion give no clue to the electronic disturbance shown magnetically. Therefore, at least in the study of some electronic changes, the thermomagnetic method is a far more sensitive one than the diffusion method described.

With respect to the changes in the isobars at 945 degrees Cent. (1735 degrees Fahr.) and between 200 degrees Cent. (390 degrees Fahr.) and 350 degrees Cent. (660 degrees Fahr.), it is felt that they can be accepted only with certain reservations until other methods confirm that they are real or unreal. This is especially true of the 950 degrees Cent. (1740 degrees Fahr.) point, since all the evidence for its existence seems to depend upon the 954 degrees Cent. (1750 degrees Fahr.) datum (Fig. 12) which, when plotted, falls only very slightly off the straight line. If the suspected changes really exist and are electronic in character, it seems plausible to expect that carefully conducted thermomagnetic or electrical conductivity studies should confirm the conclusion of the author.

Oral Discussion

C. R. AUSTIN:⁴ I am sure that it will generally be agreed that we have been very fortunate in having Dr. Ham submit to this society some of the salient features of his researches on diffusion. I understand that the author has given the subject of gaseous diffusion his attention for the past six years,

³R. M. Bozorth, "Present Status of Ferromagnetic Theory," presented at the A.I.E.E. convention, New York, January 1936.

⁴Department of Metallurgy, Pennsylvania State College, State College, Pa.

and it has been my good fortune to have the opportunity to follow the experimental work and to listen to some of the stimulating theoretical concepts of Dr. Ham during the past two years.

At first sight some of our members may consider this paper to be purely theoretical in nature and of importance only to the theoretical or academic metallurgist. However, as Dr. Mehl has recently pointed out in his Institute of Metals Lecture, the process of diffusion is important in such well known practical aspects of our subject as homogenization and rates of transformation and precipitation.

In the earlier experimental work by the author, he appeared to be particularly intrigued by the fact that the allotropic change in iron at about 900 degrees Cent. (1650 degrees Fahr.), as well as the magnetic inversion at 760 degrees Cent. (1400 degrees Fahr.), was clearly revealed by a definite change in slope of the isobar for diffusion by hydrogen through the metal. If gaseous diffusion is an electronic phenomenon this change in slope at the lower temperature is rarely understood, but a reason for the change at the alpha-gamma inversion is not so evident. Later, when Dr. Ham revealed that he had obtained a modification in the slope of the isobar at about 200 degrees Cent. (390 degrees Fahr.) it appeared to the writer that a remarkable fact had been revealed which might have important theoretical significance.

It was pointed out to Dr. Ham, who had already noted the tensile strength anomaly of pure iron at this temperature in Dr. Sauveur's well known text, that many metallurgists considered that the manifestation of this marked increase in tensile strength was due to some kind of precipitation hardening. As you all know, carbon, oxygen and nitrogen have all been selected as the cause of this low temperature hardening. The author of this paper, however, appeared to feel, that on account of the purification treatment to which the selected iron had been subject, even the purest iron would reveal this diffusion discontinuity. It was nevertheless admitted that the presence of the above mentioned elements might accentuate the effect, and it was particularly interesting to have the suggestion that the electronic shift in the iron atoms might be the cause of a marked change in solubility at the temperature of temper brittleness. Indeed the author appears to believe that all the changes previously found in pure iron are associated with sudden changes in the electronic characteristics of the atom.

Many will recall that several years ago Dr. Jeffries gave his attention to this low temperature property of iron, and expressed the view that the phenomenon must be attributed to an allotropic change. He considered that the lack of definition of the temperature inversion was due to the high mechanical cohesion obtaining at so low a temperature. It is particularly interesting to find now that a physicist ascribes the maximum in tensile strength to an electronic shift comparable in some way to that found in the magnetic inversion. Whether such changes may be regarded as examples of allotropy naturally depends on the definition of that term.

In any case there is little need to stress the industrial importance of this problem and every encouragement should be given to any one who may bring to bear such searching methods of experimental analysis of the possible fundamental explanations of the problem.

I recall the wide use of thermal analysis by Dr. Rosenhain as a means of studying phase changes and polymorphic inversions in alloys. Later came the use of dilatometric studies which unquestionably had certain advantages over the thermal method, and now we appear to have a unique method in the use of diffusion rates. As Dr. Ham has pointed out, a few minutes suffices to obtain the diffusion rates required to locate the desired temperature of electronic shift.

In general, the paper provides us with some definite conceptions of the mechanism of diffusion, and what, may be asked, is more important in the science of heat treatment, than knowledge of the process of diffusion of partially soluble disperse phases. True, the present work relates to gaseous diffusion, but our better known methods of surface hardening depend largely on gaseous diffusion. In this field it is particularly noteworthy to find that the presence of hydrogen in solution in the iron markedly increases the rate of diffusion of nitrogen.

Many more comments might be made but I shall conclude by recording the pleasure afforded me in following the work discussed in the paper and in having the opportunity to make these few comments. I trust that other papers may emanate from the author.

R. F. MEHL:⁵ Dr. Ham very kindly sent me this paper in manuscript form before it was submitted for publication, thinking I would find it interesting, as indeed I have. It is really quite unnecessary to insist upon the importance of diffusion phenomena in metallurgical behavior. The recent work on carburization including the complicated phenomena which attend the simultaneous diffusion of carbon and oxygen in iron, the recent work on flakes in forging steel, which now appear to be caused by hydrogen, the older work on pickle brittleness and pickle blisters, all point to a very important part played by the diffusion of gases in metallurgical phenomena. It is a peculiar thing that probably the philosopher and the moralist will have to explain—that Providence should have made our most useful metal our most complicated, for apart from the many complications induced in steel by the allotropic transformations in iron, the pure metal iron possesses several striking idiosyncrasies, including a maximum in the coefficient of thermal expansion below A_2 , as pointed out by Dr. C. R. Austin several years ago, a peculiar periodicity in the specific heat, as pointed out recently by Naeser in Germany, and now, from Dr. Ham's work, several remarkable peculiarities in the diffusion of hydrogen.

One of the most striking of the results obtained by Dr. Ham is the change in the slope of the curve plotting the logarithm of the rate of diffusion against the reciprocal of the absolute temperature. Since from the slope of this curve the value of Q , the heat of diffusion may be calculated—the heat representing the energy required to enable the atoms to become mobile, i.e., to diffuse, we may see from Dr. Ham's results that the value of Q changes at the Curie point. His curves show that Q is less above the Curie point than below it, a result which is not strange, for iron absorbs much energy in passing through A_2 , and thus less additional energy is required to activate the diffusing atoms. This is the first time that this has been shown, I believe, and thus Dr. Ham has added an important fact to our knowledge of diffusion.

⁵Director, Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh.

I seriously doubt that pure iron can be made to show a true hysteresis in the A_3 transformation, as suggested by several of Dr. Ham's curves. The paper presented here last year by Wells, Ackley, and Mehl showed that the difference between the A_{c3} and the A_{r3} temperatures is clearly dependent upon the rates of heating and cooling, and that it can be made as little as 2 degrees Cent. in the purest iron when these rates are $\frac{1}{8}$ degree per minute,—slower rates would doubtless bring the temperature points even closer.

Nor do I believe that the point of inflection in the diffusion curve at 300 degrees Cent. (570 degrees Fahr.) is in any way associated with blue brittleness, for we know that the temperature of maximum tensile strength in iron, i.e., the temperature of blue brittleness, is dependent upon the rate of application of load, occurring at higher temperatures at the higher rates of loading. Furthermore, we now know that blue brittleness and over-strain aging at room temperature are but different manifestations of the same process. For these reasons the temperature of 300 degrees Cent. (570 degrees Fahr.) is of no unique significance in the process of aging or embrittling.

It will be pleasant to follow Dr. Ham's work, for it is of considerable importance to metallurgy, and should be increasingly so.

W. R. HAM: I would not pretend for a moment that this was a precision research. I offered it as an illustration of what might be done in the future. I am sorry that I did not get a discussion on the point that interested me so much, i.e., the apparent equality in the temperature rise that is necessary to correct the hydrogen diffusion break in nickel, with that necessary to straighten out the cooling curve of nickel, and further with the temperature change to straighten out Hedvall's curve on the efficiency of nickel as a catalyst for an oxygen reaction, all of these breaks being at 360 degrees Cent. (680 degrees Fahr.). To me, as a physicist, that is the most significant point of the paper. I am, however, setting up precision apparatus, and I have some excellent iron that should be almost perfectly decarburized, and I hope to get further results at an early date. I also am setting up a rather elaborate electromagnetic outfit for testing the transitions in iron. I am beginning to be much interested in the peculiarities of iron, and I want to say in conclusion that I would not for a minute suggest that the diffusion method is one that will give complete enlightenment on this subject, that is, as to transitions in iron. It is necessary to get all methods available working to the best advantage, and to so correlate the results that we have a complete agreement, and this is a problem that will still take a considerable length of time.

Author's Closure

With regard to the comments of Dr. Wells, it should be noted that a dilatometer measures change of volume and the abnormal variations of volume with temperature irrespective of whether such changes in volume are or are not accompanied by atomic phase change. The same may be said of a thermal arrest apparatus. Either method can hope to show only the net result.

There is no good reason why measurements with a dilatometer should check exactly with X-ray measurements, and of course hydrogen diffusion measurements that are apparently independent of crystal aggregates or arrange-

ments, and dependent only on lattice forces, cannot be expected *a priori* to check with either.

And as to the method best suited to an investigation of transition, it seems to the author that the choice depends upon what one wishes to know about such transformations. If one is investigating a phase change proper, e.g., body-centered cubic to face-centered cubic, the X-ray analysis should be most reliable. If one wishes to follow the electronic shifts in the atoms that finally lead to the change just mentioned, hydrogen diffusion is a very sensitive method. A dilatometer may be better adapted to practical problems than either the X-ray or the diffusion method, since it evidently detects both types of transformation as is shown by observation on both the Curie region and the body-centered—face-centered cubic region of iron.

And with regard to thermomagnetic measurements it may be remarked that although a magnetic field itself, as has been mentioned by the author in other reports, has no observed effect on the diffusion of hydrogen, the electronic shift in particular atoms that bring about the Curie change has a marked effect and the region of such change can easily be followed. One must not confuse the gross effect, i.e., magnetic interactions throughout the crystal, which apparently do not affect hydrogen diffusion, with the electronic shifts in individual atoms which do alter the diffusion rate. These remarks apply to the whole magnetic discussion of Dr. Wells. One might note that in referring to recent ferromagnetic theory the name of Dr. Slater should have been included.

The sensitivity of the hydrogen diffusion method is not confined to the detection of any one type of electronic shift; the method has been found satisfactory for the shifts which are ultimate cause of the beta-gamma transformation and for shifts which are directly responsible for the alpha-beta transformation. (For instance, in changing from the gamma state to the beta state, the abnormal change in the diffusion rate of hydrogen is about 100 per cent. The corresponding change in dilatometer readings is about $\frac{1}{2}$ per cent). The diffusion method appears to be sufficiently sensitive, too, for still other types of electronic shifts in iron.

Turning to the discussion by Dr. Austin, it does seem that the low temperature transition, 200-350 degrees Cent. (390-660 degrees Fahr.), may be quite important, particularly as it still persists, although probably less marked, as traces of carbon are removed. The author feels with Dr. Wells that this point needs much more experimental investigation before certain conclusions are drawn. To investigate this by hydrogen diffusion is a slow process, one must wait so long to obtain a steady state at these low temperatures.

Concerning the discussion by Dr. Mehl—again I would say that the question of approximate coincidence between A_{c_2} and A_{r_2} points would not be answered with certainty either by hydrogen diffusion or by the dilatometer. The X-ray spectrograph apparently is the only available tool for answering this question. The hydrogen diffusion isobars do show the nature of the lattice force changes which eventually lead to the body-centered—face-centered transformation and there is certainly considerable hysteresis* as well as a temperature range of

*Later: Since writing the paper this is found to apply to some of the purest iron used by Dr. Mehl and others in the dilatometer.

approach much larger than is indicated either by X-ray analysis or the dilatometer in all relatively pure iron samples available.

Concerning Dr. Mehl's discussion on the low transition point, I am of quite open mind. Further investigation should be interesting. At present it appears that the break between 200-350 degrees Cent. (390-660 degrees Fahr.) is less marked with increasing decarburization, which might support Dr. Mehl's contention as to the fundamental cause of the marked physical changes observed in the region mentioned.

In conclusion, I might say that one point brought out by Dr. Austin seems particularly important. In metallurgical discussion more than in most other lines, it seems necessary to very carefully agree on definitions of terms before starting the discussion.

CADMIUM-SILVER-COPPER ALLOYS FOR ENGINE BEARINGS

BY C. F. SMART

Abstract

Data from laboratory tests indicated that the ternary alloys of cadmium-silver-copper possessed desirable properties for bearing metal. Bearings tested in engines under severe operating conditions showed approximately three times the life of babbitt bearings. The alloy offers no particular manufacturing difficulties.

Comparative data for a number of alloys of cadmium with other metals are given.

ENGINE design and manufacture, for highly practical reasons, must be a compromise of factors involving materials, manufacturing limits, costs, and the relationship of part to part. Given theoretically ideal design, with perfect lubricating films between moving parts, then the special alloys which we class as bearing materials would not be essential. However, with the practical limitations always present in engine construction, the variations in clearances between shafts and bearings, the deflections of materials under load, the heat generated by friction and combustion, and the difficulty of maintaining 100 per cent film lubrication, then the proper functioning of a bearing alloy is essential to successful engine performance. Thus bearing material acts as a bridge over the gap between theoretical perfection and the practical deficiencies of design and manufacture; its function to prevent heating, galling or seizure, or excessive wear between metal parts working at high load, high speed and close tolerances.

Because of their importance, automotive bearings and bearing materials have received considerable attention from engineers and metallurgists. The alloys most commonly used for connecting rod and crankshaft main bearings have been the lead-base and the tin-base babbitts. Alloys of cadmium have recently been developed which have shown certain advantages for bearing purposes. It is the purpose of this paper to present data from laboratory work on

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the cadmium alloys, and the results of practical engine tests of bearings made from them.

The requirements for a successful bearing material have been hinted at in the definition already given. They may be enumerated as follows:

1—Low frictional characteristics in contact with shaft materials.

2—Freedom from any tendency to abraid, gall or seize the shaft upon which they contact.

3—Strength and toughness throughout the operating temperature range (from below 0 to 300 degrees Fahr. and higher) sufficient to satisfactorily carry the imposed loads and deflections, without excessive plastic flow, cracking, or unduly early fatigue failure.

4—Capacity to bury abrasive particles, metallic or non-metallic, which may contaminate the lubricating fluid and pass between bearing and shaft.

5—Resistance to corrosion by lubricating fluids, or products which may be developed in these by use.

6—The ability to be practicably manufactured into close tolerance bearings, involving such considerations as the temperature required for casting, formability in dies, ability to be strongly bonded to backing materials, suitable machining properties, and cost.

The materials used for automotive engine bearings represent such compromises between these various factors as may appear desirable under a given set of conditions, no one of the several commercially available materials best meeting all of them.

The tin-base babbitts have been most widely used, and, in general, have in the past been quite successful. They represent long experience, covering a range of compositions and manufacturing practices. Much work has been done with them, both in laboratory and plant, to study the effect of the variables of analysis, casting practice, bonding, cooling rate, macrostructure and microstructure, on the ultimate serviceability of these alloys. Naturally, based on accumulated experience, there exists some disagreement in individual practices. However, these studies resulted in decided improvement in the life of babbitt bearings and pointed out, among other things, the importance of freedom from brittleness, freedom from low

melting point constituents, and the necessity for high bond strength between the bearing metal and the back.

In general, these alloys have been particularly good as regards low frictional characteristics and freedom from wearing or galling of shafts. The principal disadvantage of the tin-base babbitts is their susceptibility to fatigue failure at elevated operating temperatures. The life of babbitt bearings has become less as operating speeds, loads,

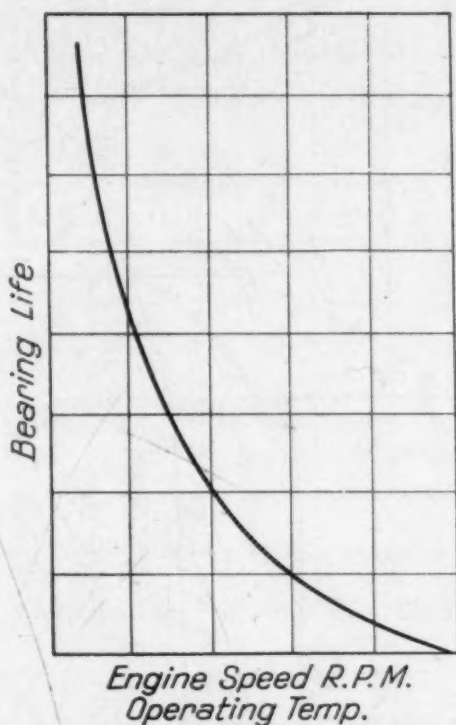


Fig. 1—Hypothetical Curve of Bearing Life Plotted Against Operating Temperatures or Engine Speeds.

and temperatures have been increased through the general trend in engine design to higher revolutions per minute and higher power output per unit of weight.

Much of the work that has been undertaken on babbitt bearings has been with a view to improving this condition of early fatigue failure. Likewise the use of light metal reciprocating parts has been influenced by the desire to decrease bearing loads and improve bearing life. Fig. 1 represents a hypothetical curve of bearing life plotted against operating temperatures or engine speeds. As engine speeds increase, bearing loads increase through the inertia effect of reciprocating parts, temperatures increase due to higher loads and

more frequent explosions. On the other hand, bearing metal strength decreases as temperature increases, becoming nil at the melting point of any continuous constituent. The resultant of these factors is a sharply decreasing bearing life with increasing speeds and temperatures.

Working toward possible improvement of bearing life, the possibilities of alloys other than lead-base or tin-base materials had re-

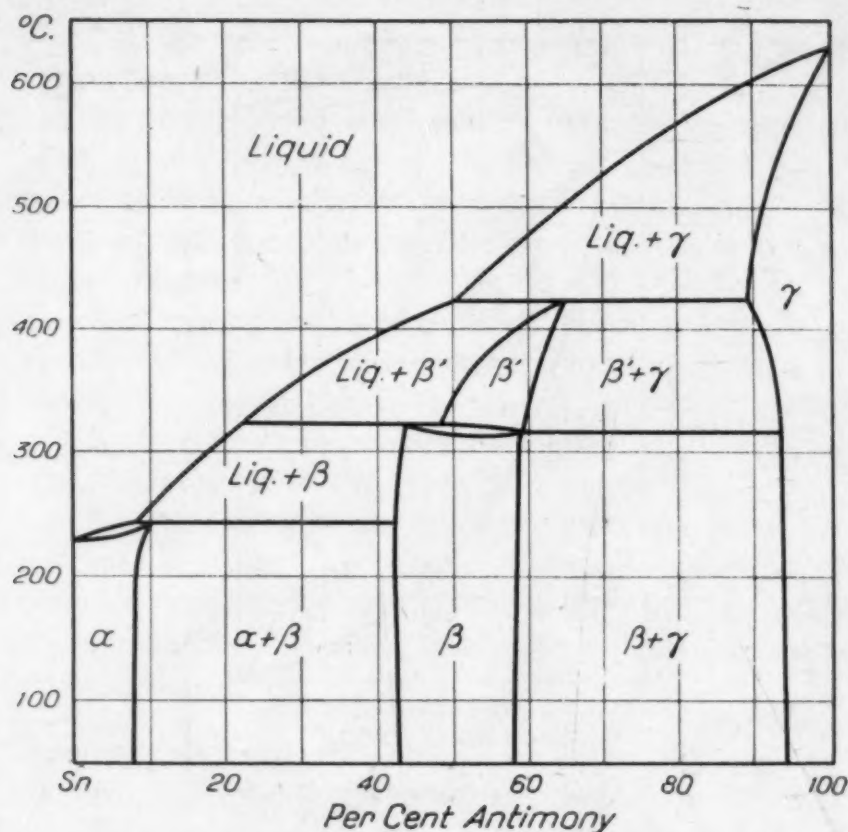


Fig. 2—Tin-Antimony (Iwase, Aoki and Osawa, Science Reports Tohoku Imperial University, 1931, v. 20, p. 353.

ceived some attention. The alloys of cadmium offered promise due to the known low frictional effect between cadmium and steel. Cadmium offered the advantage of high melting point, (610 as compared to 450 degrees Fahr. for tin) and greater strength than either tin or lead. Accordingly, we could assume that some of the alloys of cadmium would offer improvement in the fatigue life of bearings, although some of the cadmium alloys were known to have been tried with rather unsatisfactory results.

Familiarity with the structural composition of babbitt metals led to considerations of the possibility of similar structural features

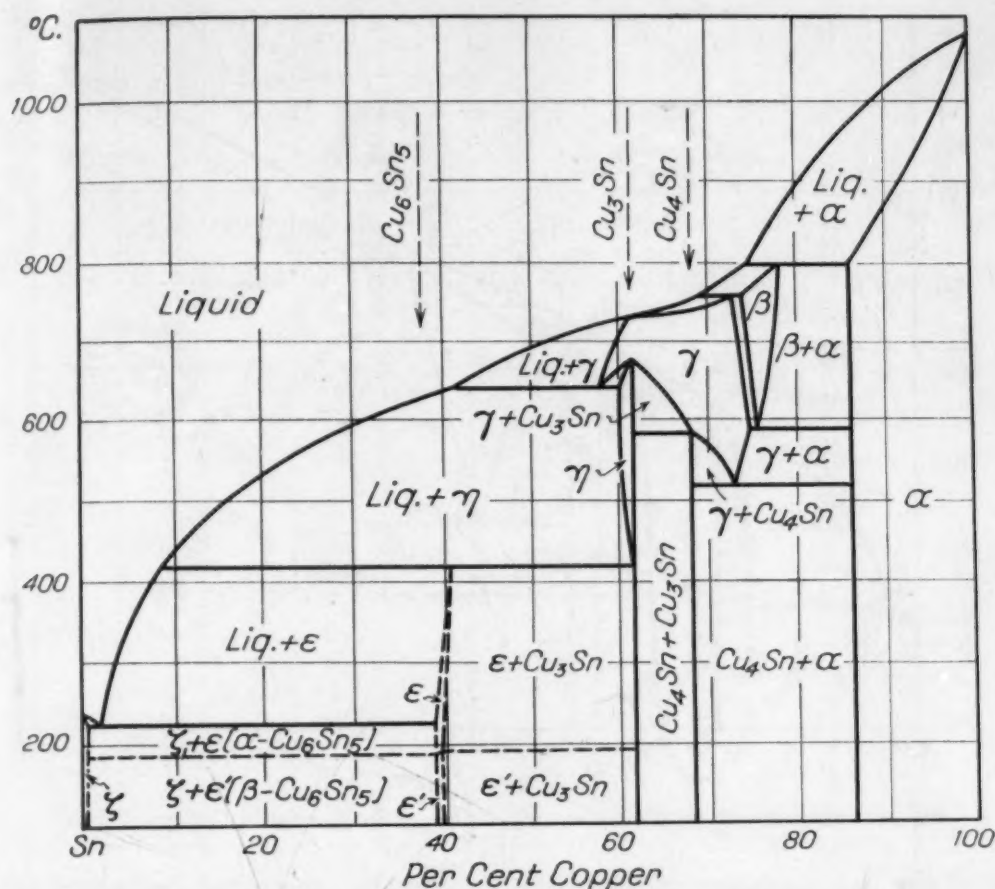


Fig. 3—Tin-Copper (Bauer and Vollenbruck, Mitt. Material, 1922, v. 40, 181; Z. Metalk., 1923, v. 15, p. 119, 191).

for cadmium alloys. The published structural diagrams of cadmium alloys, therefore, indicated a line of investigation—to select a metal which would form a suitable solid solution alloy with cadmium corresponding to the solid solution of antimony in tin, and to select a secondary hardening element which might give effects corresponding to the effect of copper on the tin-antimony alloy. Based on such considerations, the solid solution of silver in cadmium—reinforced by a secondary metallic component produced with copper, antimony, or nickel—appeared as the logical alloys which might be expected to meet the desired physical requirements.

Figs. 2 and 3 reproduce the structural diagrams of tin-antimony and tin-copper. Figs. 4 to 13 reproduce the structural diagrams of cadmium-silver, cadmium-copper, cadmium-antimony, cadmium-nickel, cadmium-lead, cadmium-zinc, cadmium-tin, cadmium-mercury, and cadmium-magnesium. The similarity between the cadmium-silver

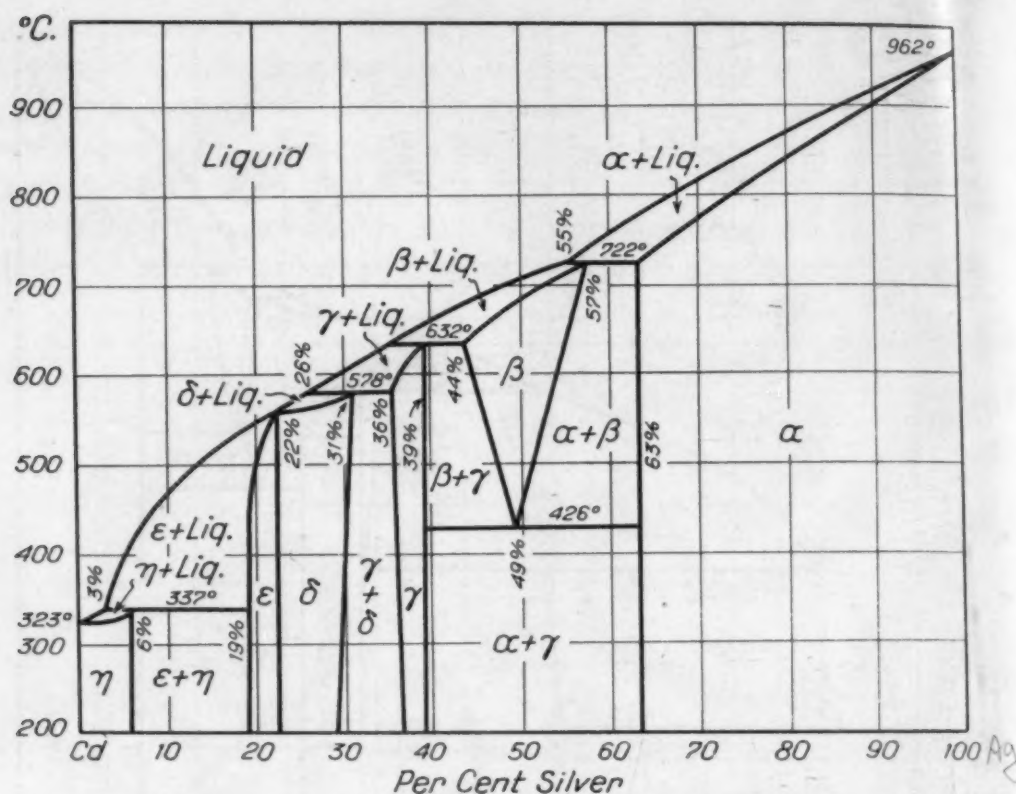


Fig. 4—Cadmium-Silver (Petrenko and Federov, International Critical Tables).

and the tin-antimony diagrams is noteworthy, as is that between cadmium-copper and tin-copper, the former showing solid solutions, and the latter eutectics, in the cadmium-rich and tin-rich alloys respectively.

Alloys of cadmium-silver, cadmium-copper, and cadmium-silver-copper, covering a considerable range of silver and copper content, were made in the laboratory and checked for hardness, hot and cold bending, the effects of annealing and cold working, and were examined under the microscope for structure.

The properties of these alloys indicated that from them might be selected compositions which would be excellent to meet the various requirements of bearing metals. Bearings made from cadmium-silver-copper alloys have confirmed this in practice. A number of alloys of cadmium with other metals were likewise made and tested for comparison. The alloys were prepared by melting cadmium in an iron crucible, using a covering of zinc chloride to avoid undue oxidation. The cadmium was of the grade supplied for commercial electro-plating. To the molten cadmium was added the secondary metal or metals, heating and stirring the bath until complete

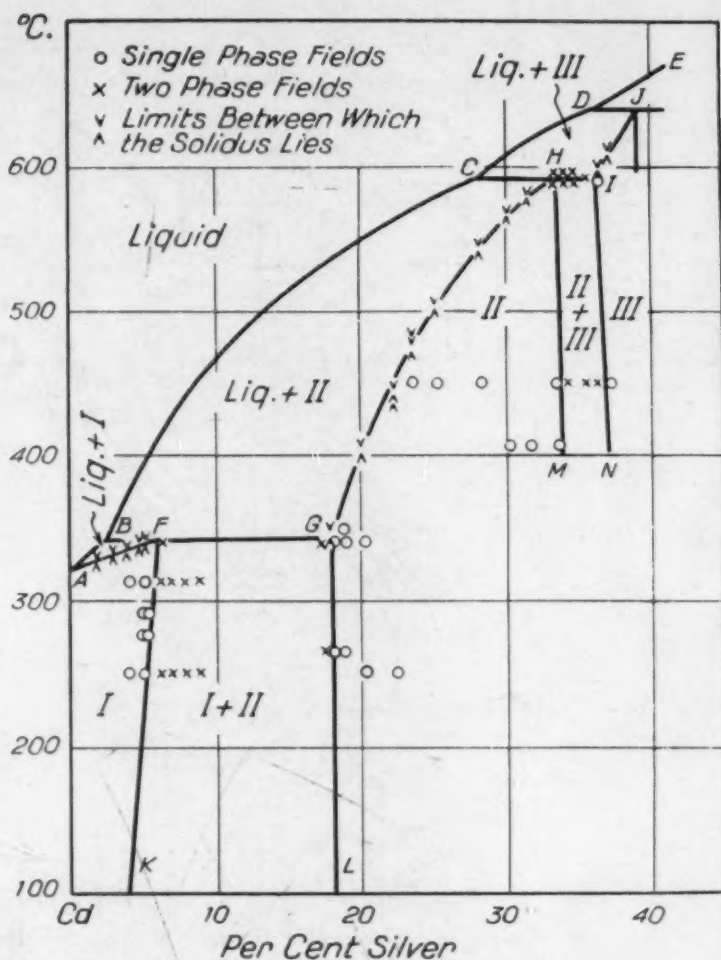


Fig. 5—Cadmium-Silver (Durrant,¹ *Journal, Institute of Metals*, 1931, Vol. XLV).

solution had taken place. (Such metals as silver and copper in thin strips dissolved quite readily in the molten cadmium at temperatures not exceeding 850 degrees Fahr. In the case of metals which were lighter than cadmium, the additions were held submerged with an inverted steel cup. A pine stick used for stirring acted as an excellent deoxidizing agent, and the carbonaceous material which separated floated to the surface of the bath, and mixing with the liquid zinc chloride, thickened the covering so that it could be easily skimmed aside for pouring. The melts were cast at approximately 750 to 800 degrees Fahr. into sheet steel molds, to give flat castings $1\frac{1}{2} \times \frac{1}{2} \times \frac{3}{8}$ -inch thick. In the majority of instances these were cooled rapidly to produce an effect approaching that which might be expected in the commercial casting of bearings in centrifugal casting operations. Some were purposely cooled slowly by preheating the molds,

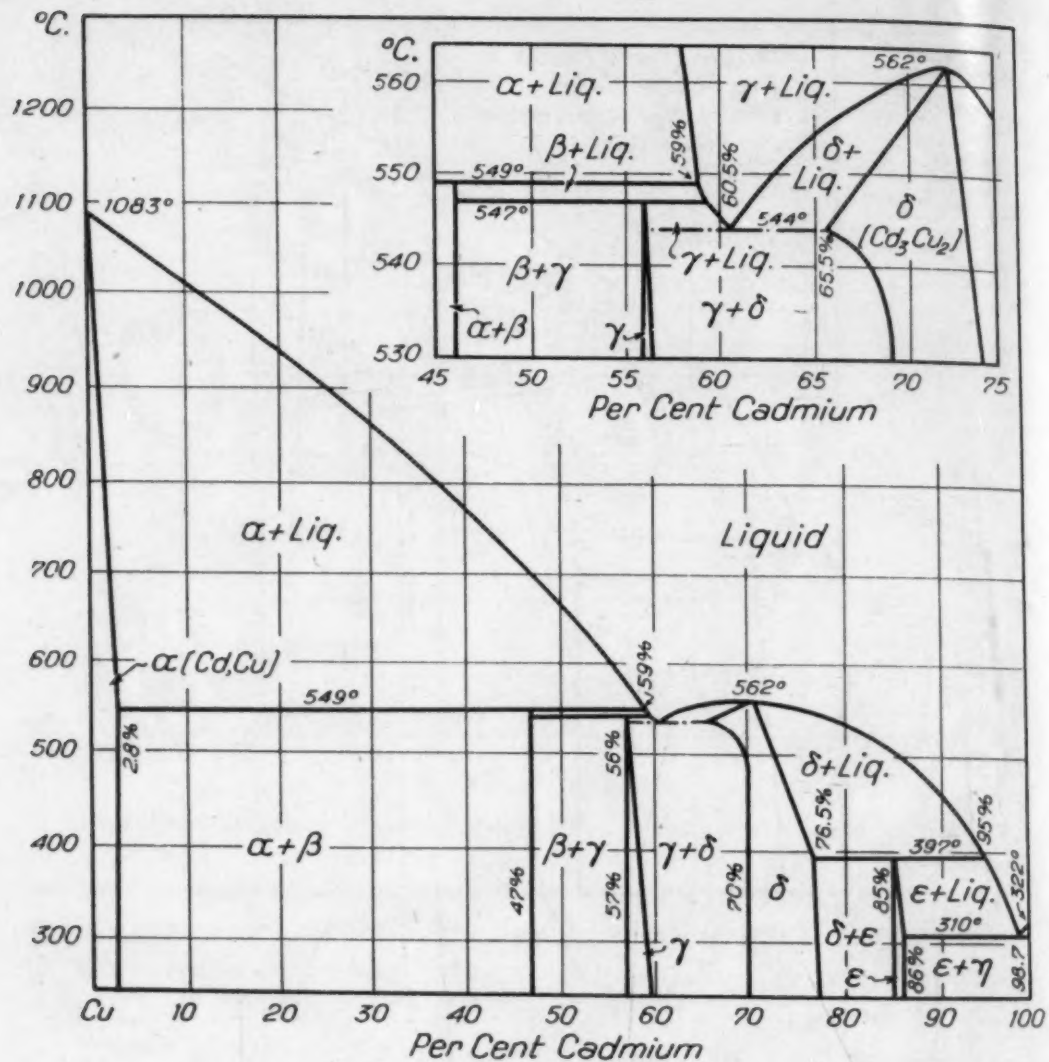


Fig. 6—Cadmium-Copper, (Jenkins and Hanson,* *Journal, Institute of Metals*, 1924, Vol. XXI).

in such instances as the effect of the rate of cooling was to be studied. (In general, with tin-base babbitts, experience has indicated that greatest strength, toughness and bearing life resulted from the fastest practical cooling rate, using compressed air, and sometimes water spray to accelerate cooling.) The cast sections were checked for Brinell hardness, using a 10-millimeter ball and 500-kilogram load applied for 30 seconds, first grinding a smooth flat surface on the face of the billet. Bending tests were made by clamping the test specimen in a vise and bending over the free end by hammering, noting the angle of bend required for the development of cracks or fracture. The same procedure was followed for hot bend tests ex-

cept that the samples were heated in an oil bath at 400 degrees Fahr. and bent as rapidly as possible on removing from the bath. Considering that the angle of bend to produce failure ranged from zero degrees to no failure whatever when specimens were bent double and hammered flat, this test was believed to disclose sufficient informa-

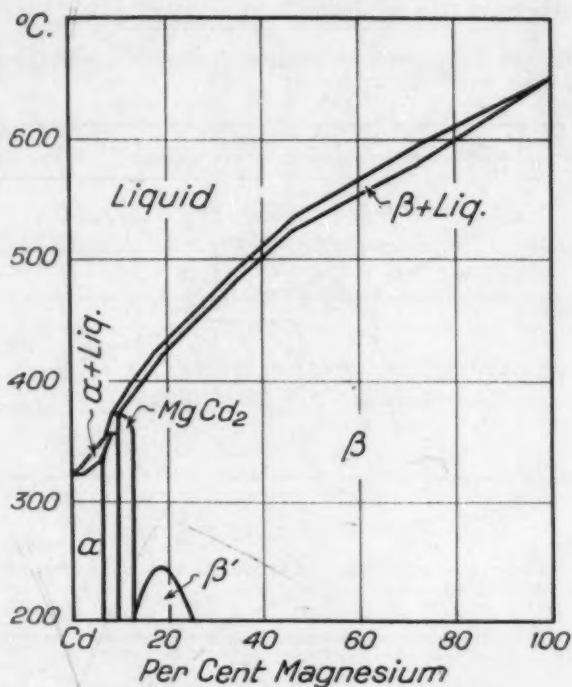


Fig. 7—Cadmium-Magnesium (Hume-Rothery and Rowell, *Journal, Institute of Metals*, 1927, Vol. XXXVIII).

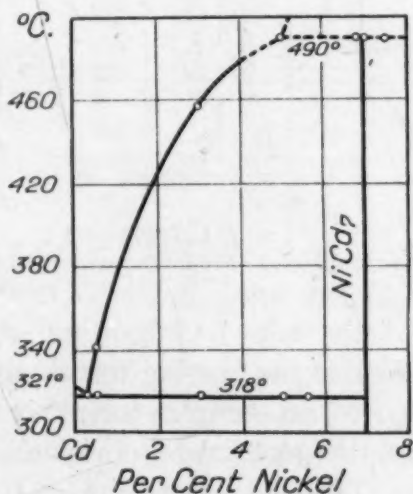


Fig. 8—Cadmium-Nickel (Swartz and Phillips, *A.I.M.E.*, 1934, III, p. 334).

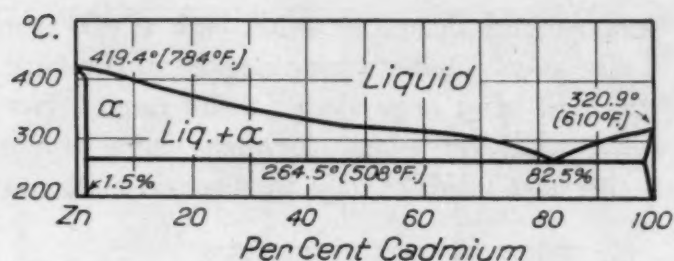


Fig. 9—Cadmium-Zinc (Peirce, National Metals Handbook, 1933, p. 1423).

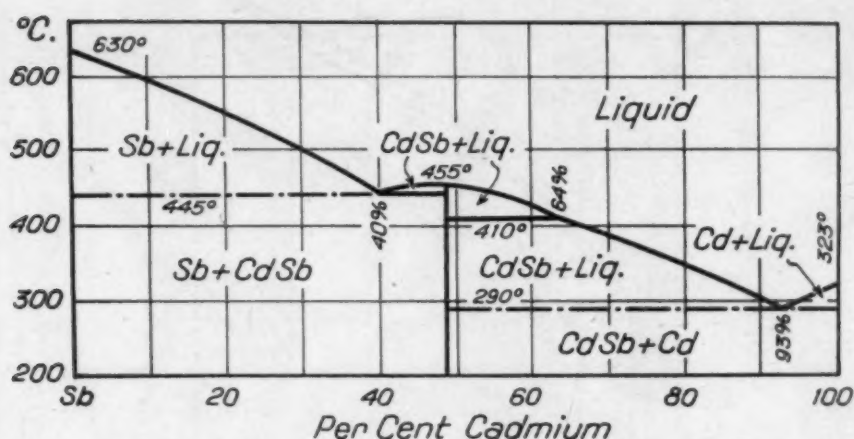


Fig. 10—Cadmium-Antimony (Kurnakov and Konstantinov, International Critical Tables).

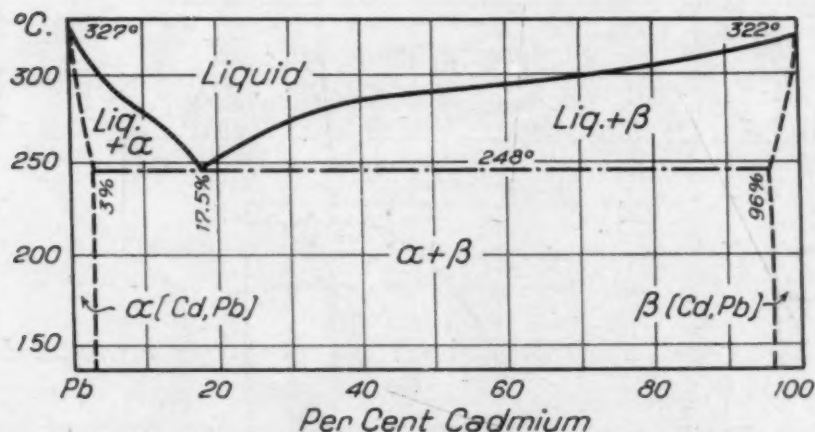
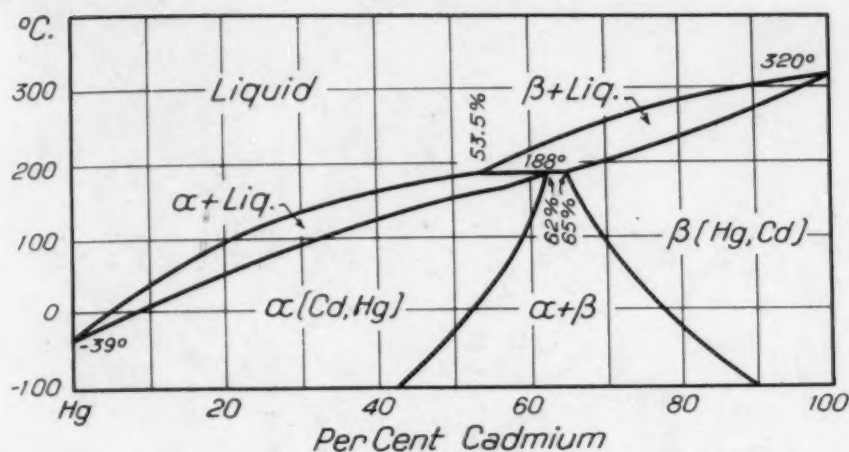
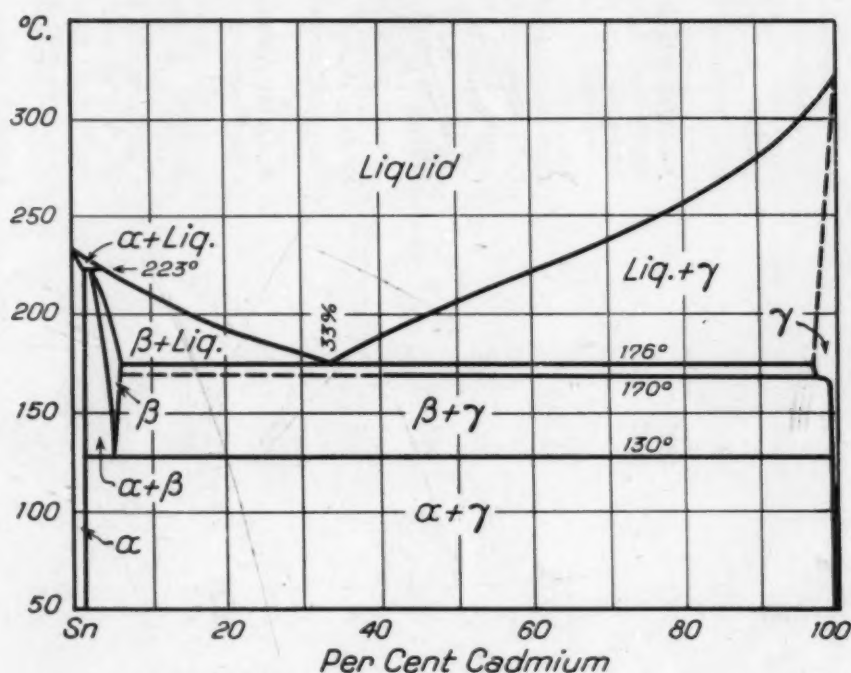


Fig. 11—Cadmium-Lead, (Baar,² International Critical Tables).

tion on the ductility of the alloys to indicate which possessed the toughness considered suitable for bearing metal purposes. The effect of cold work was observed on samples hammered on an anvil to a predetermined thickness, the percentage of reduction being expressed on the thickness ratios. Thermal treatments at 210 and 340 degrees Fahr. were carried out in standard electrically heated laboratory ovens. Thermal treatments at higher temperatures were conducted

Fig. 12—Cadmium-Mercury (Brijl,² International Critical Tables).Fig. 13—Cadmium-Tin (Hanson-Pell-Walpole, *Journal, Institute of Metals*, 1935, 56; 1936, 58).

in a Homo furnace. The data obtained from these tests are presented in tabular form arranged in groups according to composition. See Table I.

The Brinell hardness of a sample of cadmium melted and cast in the above manner was determined as 23-24, which checks with published data. Bend tests on cast cadmium showed no cracking at 180 degrees, either hot or cold, the surface taking on a wrinkled appearance. The tensile strength of cast cadmium is reported as 13,660 pounds per square inch with 44 per cent elongation on a 3-inch gage

Table I
Composition and Physical Properties

Alloy Group	Composition Per Cent	Brinell As Cast	Cold Bend	Hot Bend	Treatment	Brinell	Bend
Group I 1-1	Cd. 100	23	180°	180°			
	Cd. Ag.	28.3	180°		Cold hammered 50%	24.9	
	2-1	33	180°		Annealed 66 hrs. at 340° F.	34.5	
	2-2	34.5	180°		Rolled from 0.250" to 0.090"		
	2-3	36	180°		Annealed 1 hr. at 400° F., rolled to 0.020"		
Group II 2-4	2.39						
	2.88	36	180°		Cold hammered 33%	46	
	6.0	36-40	60° Fr.		Cold hammered 33%, 400° F. 15 min. water cool.	30	
Group III 2-7	12.0	57	45° Fr.		Cast section 1½ hrs. at 575° F. water cool	34.5	
	Cd. Cu.				400° F. air cool	50-52	Brittle
	0.10	31-33	180°		16 days at 210° F.	24	180°
	0.125	34.5	180° Cr.		Cast, cold hammered 40%	34.5	90° Tore
	0.20	34.5	135° Cr.		Annealed 114 hrs. at 340° F.	28.3	
Group III 3-1	0.50	38.0	180° Cr.		Cold hammered 50%	42.5	
	0.75	38-40	135° Cr.		Annealed 3 hrs. at 575° F., water cool	40	180°
	1.00	42.5	60° Cr.		Cold hammered 50%	32.6	
Group III 3-3					114 hrs. at 340° F.	33.5	
					2 months at room temp. (casting)	38	
					24 hrs. at 340° F.	36.1	
Group III 3-6					Probably porous casting		
Group III 3-7	1.20	43.7-44.8	45° Cr.				
	1.50	42.5	10° Cr.				
	5.53 (a)	33	0°				

Fr.... fractured. Cr.... cracked. (a)....by chemical analysis, otherwise according to mixture.

Table 1 (continued)

Alloy Group IV	Composition Per Cent			Brinell As Cast	Cold Bend	Hot Bend	Treatment	Brinell	Bend
	Cd.	Ag.	Cu.						
4-1		0.50	0.50	40	135° Cr.	180°	Annealed 575 °F.	45	135° Cr.
4-2		1.00	1.00	47.5	60° Cr.		Annealed 42 hrs. at 340° F.	40.1	
4-3		1.00	1.25	42.5			Annealed 7 days at 340° F.	38	90° Fr.
							400° F. and air cooled	38	180° Cr.
4-4		1.25	0.75	42.5	135° Cr.				
4-5		1.42	0.15	36			Remelted		
4-6		1.50	0.50	42.5	135° Cr.		3 hrs. at 550° F., water cool	38	45-60° Fr.
4-7		1.75	0.25	38	180°		oven cool	45	5-10°
4-8		1.75	1.15	47.5	5-10° Fr.		Cold rolled from 0.760" to 0.187", Tore at last pass	45	5-10°
4-9		1.80	0.21				Annealed 1 hr. at 400° F.	23	90° Tear
							Rolled to 0.090", annealed 1 hr. at 400° F.	33	180°
4-10		1.88	0.24	38			Rolled to 0.020"		
							Cold hammered 5/8" to 1/4"	36	
							Cold hammered 1/4" to 1/8" (no anneal)		
							1/8" annealed 16 hrs. at 210° F.	27.2	135° Tear
4-11	2.00	0.20		40				31.2	180° O.K.
4-12	2.24	0.26		45					
	2.39	0.24					Cold hammered 3/4" to 3/8"	45	
4-13				42.5	90° Fr.		Cold hammered to 1/4"	30-32.5	
							Annealed 210° F.	38	
4-14	2.52	0.26		45	135° Cr.		3 hrs. at 350° F.	38	180°
							4 days at 350° F.	38	
							Cold hammered 40%	50	
4-15	2.88	0.124		42.5	90° Fr.		Cast-annealed 48 hrs. at 210° F.	38	
							Cast-annealed 113 hrs. at 210° F.	36	
4-16	2.80	0.29 (a)		45	90° Cr.		Cast-annealed 166 hrs. at 210° F.	38	
4-17	2.88	0.248		45	45° Fr.				

Table I (continued)

Alloy	Composition Per Cent			Brinell As Cast	Cold Bend	Hot Bend	Treatment	Brinell	Bend
Group IV (continued)									
4-18	Cd.	Ag.	Cu.	42.5	180°		3 months at room temp.	42.5	
4-19		2.81	0.31	45			Cold hammered 33%	50	
		3.00	0.30				Cold hammered 33%, annealed 66 hrs. at 210° F.		145° Cr. (1/4")
4-20		5.00	0.49 (a)	50	75° Cr.	180°	Severely cold hammered	38	
							Severely cold hammered, annealed 400° F., air cool	70	
							Cast-annealed 400° F., air cool	47.5	
4-21		6.00	0.25	47.5	30° Fr.			47.5	
4-22		6.00	0.50	50.0	30° Fr.		575° F. 6 hrs. water cool	50	45° Fr.
4-23		6.00	0.75	53.5	20° Fr.				
Group V									
5-1	Cd.	Mg.		29-31	180°		Cold hammered 50%	26	
		0.10					Cast, 2 hrs. at 550° F., water cool	26	Brittle—Coarse
5-2		0.37-0.39 (a)		54	Very Brittle	180°	Cast, 2 hrs. at 550° F., oven cool	26	180°—Tough
5-3		2.64-2.71 (a)		58	90° Fr.		35 days at room temp.	Very Brittle	
							35 days at room temp.	50	Brittle
							35 days at room temp. 575° F. 1 1/2 hrs. water quench	60.5	
							400° F., air cool	50	
							Cold hammered 33%	38	
							Cold hammered 50%	32.5	135° (1/8")
							Cold hammered 50%, reheated 400° F.	45	
							Cold hammered 50%, reheated 575° F. water cool 1 1/2 hrs.	64.5	90° Fr.
5-4		5.18 (approx.)		50	Very Brittle				
Group VI									
6-1	Cd.	Cu.	Mg.	36-38	180°		Annealed 16 days at 210° F.	23	180°
		0.125	0.10				Cold hammered 40%	24-25	90° (Tore)
Group VII									
7-1	Cd.	Ni.		36.1	10° Fr.		Annealed 19 1/2 hrs. at 340° F.	31	
		1.13					Annealed 67 hrs. at 340° F.	31	Brittle

Table I (continued)

Table 1 (continued)

Table 1 (continued)

Alloy	Composition Per Cent				Brinell As Cast	Cold Bend	Hot Bend	Treatment	Brinell	Bend
Group XIII (continued)	Cd.	Ag.	Cu.	Zn.						
13-6		1.71	0.49	1.86	45	5-10° Brittle Crumbly		47 hrs. at 210° F. 408 hrs. at 210° F.	45 45	180°
13-7		2.50	0.25	5.00	45	Brittle				
13-8		1.50	0.30	12.5	53	90° Cr.				
13-9		1.50	0.43	13.9	57	45° Fr.	90° Fr.	Cold hammered 40%, 48 hrs. at 210° F. Cold hammered 40%, 408 hrs. at 210° F. Cold hammered $\frac{1}{8}$ " to $\frac{1}{16}$ " Cold hammered $\frac{1}{8}$ " to $\frac{1}{16}$ " Cast, 1 hr. at 475° F., water cool 23 hrs. at 340° F.	43.5 42.5 54 38 60.5 36	180°
13-10		0.60	0.10	21.8	53.5	Brittle				
Group XIV	Cd.	Sb.			36	Brittle				
14-1		6.67								
Group XV	Cd.	Ag.	Sb.		31	45° Cr.				
15-1		1.44	0.44		38	Brittle				
15-2		1.00	3.00							
Group XVI	Cd.	Ag.	Cu.	Sb.	38	60° Fr.				
16-1		1.75	0.25	0.25						
Group XVII	Cd.	Ag.	Cu.	Pb.	30	45° Cr.	160° Cr.			
17-1		0.93	0.05	2.66	36.1	10-20° Fr.	90° Fr.			
17-2		2.00	0.15	2.65	36	10-20° Fr.	180°			
17-3		1.85	0.10	5.33	34.5	90° Cr.	90° Fr.			
17-4		2.00	0.20	10.8						
Group XVIII	Cd.	Ag.	Cu.	Ni.	Sb.	10° Fr.				
18-1		2.5	0.25	0.38	46					
Group XIX	Cd.	Sn.								
19-1		0.05								
Group XX	Cd.	Ag.	Cu.	Sn.	42.5	Brittle	Brittle			
20-1		1.95	0.25	0.05						
20-2		2.88	0.25	0.20						
Group XXI	Cd.	Cu.	Hg.		32.5	180°				
21-1		0.125	0.42							
Group XXII	Cd.	Ag.	Cu.	Hg.	42.5	90° Fr.				
22-1		2.50	0.25	0.25						
(Coarse Crystalline)										

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length (5).* Jenkins (3) (4) reports 11,850 to 12,400 pounds per square inch tensile and 38 to 65 per cent elongation; 24-25 Brinell hardness on 1-inch round cast test bars.

The addition of silver to cadmium resulted in a uniform increase in hardness up to 36 Brinell at approximately 2.50 per cent of silver. Beyond this point the hardness was further increased, but

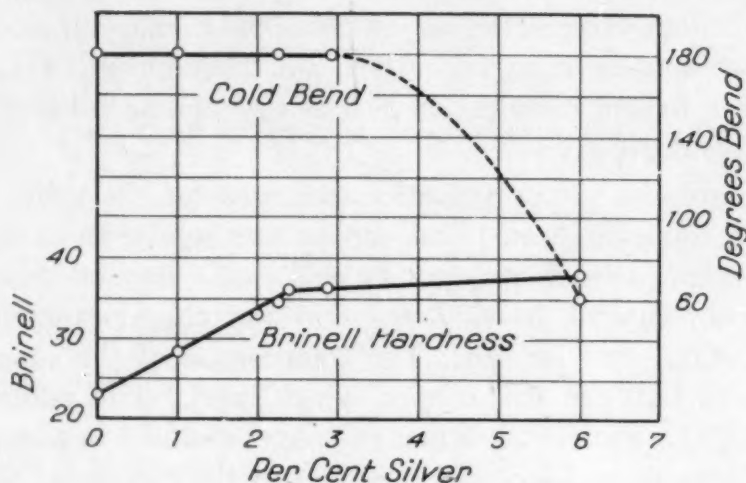


Fig. 14—Hardness and Cold Bend Cadmium-Silver Alloys as Cast.

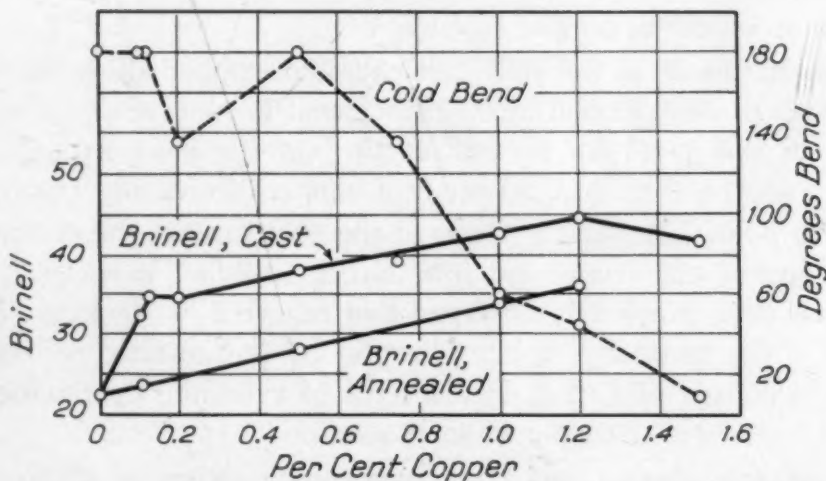


Fig. 15—Hardness Cadmium-Copper Alloys, as Cast and Annealed. Cold Bend Cadmium-Copper Alloys, as Cast.

at a lesser rate, up to 38 Brinell at 6 per cent silver. Data are shown plotted in Fig. 14. The ductility, as indicated by bend tests, was very good with silver ranging up to about 3 per cent. The microstructures of these alloys as cast showed a solid solution up to 2.50

*The figures appearing in parentheses refer to the bibliography appended to this paper.

per cent silver, and a second constituent, present in rounded rather massive particles, beyond this point. Published structural diagrams indicate that silver is soluble in cadmium up to 4 to 6 per cent (1). However, annealing the alloys containing over 2.50 per cent silver did not result in absorption of the secondary constituent, within the limits of annealing of this work (6 hours at 575 degrees Fahr., or 66 hours at 210 degrees Fahr). The only observed effect of annealing on cadmium-silver series as cast was the homogenization of the cored solid solution crystals. Alloy 2-3, containing 2.25 per cent silver, had a Brinell hardness of 34.5 as cast and as annealed for 66 hours at 340 degrees Fahr.

The hardness values and microstructures of the alloys of cadmium with copper indicated that copper was soluble in cadmium up to a maximum of 0.125 per cent as chill cast. Beyond this amount of copper an eutectic of solid solution and copper-cadmium compound (CuCd_3) was formed. The composition of the eutectic was very close to 1.20 per cent copper, which checks with published information (6). Further additions of copper resulted in alloys with a matrix of eutectic and secondary crystals of the compound separated in massive particles. The eutectic appeared in some samples as very finely divided particles, and in others as quite coarse, dependent on the rate of solidification and cooling.

The hardness of the chill cast cadmium-copper alloys increased rapidly up to 34.5 Brinell at 0.125 per cent copper, and at a slower rate from this point up to 44.2 at the eutectic composition. The ductility was good up to 0.50 per cent copper, decreasing rapidly beyond this point. Annealing changed the structure of the eutectic by coalescence of the compound into larger rounded particles. This effect has been previously observed and reported by Jenkins (3) as follows: "On annealing, spheroidization of the eutectic occurs and the alloys consist of CuCd_3 in a matrix of cadmium containing less than 0.10 per cent of copper in solid solution."

Annealing also caused a complete precipitation of the copper-cadmium compound which appeared to be held in solid solution in the rapidly cooled casting. This occurred with an annealing temperature of 210 degrees Fahr. Such precipitation and coalescence resulted in a decided softening (approximately 8 to 10 points Brinell for alloys containing 0.125 per cent and over of copper) and an increase in ductility, the alloy with 1.00 per cent copper showing good ductility after annealing. Physical test data are shown plotted in

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Fig. 15. Data on tensile strength, Brinell hardness and per cent elongation reported by Jenkins (3) for cast cadmium-copper alloys are plotted in Fig. 16.

The alloys of cadmium with both silver and copper exhibited properties and structures which might be expected from the characteristics of the binary alloys. The solid solution of cadmium-silver

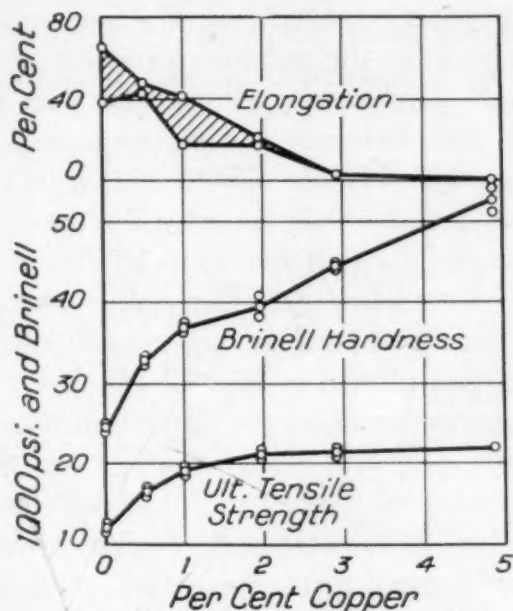


Fig. 16—Physical Property Data Reported by Jenkins, *Journal, Institute of Metals*, 1925, Vol. XXXIV, for Cast Cadmium-Copper Alloys.

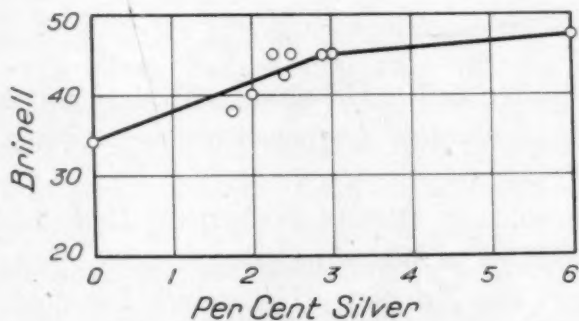


Fig. 17—Hardness, Cadmium-Silver Alloys, With $\frac{1}{4}$ Per Cent Copper as Cast.

was hardened and strengthened by the copper held in solution in the rapidly cooled casting, and by the eutectic of cadmium and cadmium-copper compound. The Brinell values were higher than for either of the corresponding binary alloys, and the ductility was very good up to the point where brittleness imparted by copper made itself

manifest. Annealing showed the softening and toughening effect due to precipitation and coalescence of the cadmium-copper compound. However, these alloys appeared to be more resistant to softening by annealing than the binary cadmium-copper alloys indicating the possibility of greater retention of copper in solution in the presence of silver. The hardness of the primary crystals (apparently a solid solution of silver and copper in cadmium up to 2.50 per cent silver and 0.125 per cent copper) ranged from the hardness of either binary alloy, up to 42 Brinell for the maximum concentration of silver and copper in solution. Higher copper content than this resulted in further hardening with decrease in toughness, and the presence of eutectic in the structure. Higher silver resulted in slight increase of hardness and the second solid solution of cadmium-silver in the structure. Again, annealing (within the limits of this work) did not result in solution of silver above 2.50 per cent. The Brinell hardness range of the cadmium-silver-copper alloys containing about $\frac{1}{4}$ per cent of copper is shown plotted in Fig. 17.

The effect of temperature on the Brinell hardness of an alloy of the composition $1\frac{3}{4}$ per cent silver and $\frac{1}{2}$ per cent copper was checked by heating samples for test in an oil bath, holding at the desired temperature for 30 minutes and making a Brinell impression with the samples submerged in the heated oil. The hardness results so obtained were as follows:

Temperature	Brinell Hardness (10 mm. ball, 500 kg.)	
Room	3.80 mm.	42.5 Brinell
225° F.	4.70 mm.	27.0 Brinell
260° F.	5.40 mm.	20.1 Brinell
310° F.	5.90 mm.	16.5 Brinell

These data are plotted in Fig. 18 along with data for the hardness of tin-base babbitts at elevated temperatures as reported by Ellis and Karelitz (7).

Fig. 19 represents an attempt to chart the Brinell hardness values for the various alloys of cadmium-silver-copper up to 8.0 per cent silver and 1.2 per cent copper. The values for cold bend test are indicated below the hardness value for each alloy tested. The copper ordinate was chosen as ten times the silver ordinate spacing in order to better show the decided hardening effect of small amounts of copper.

Fig. 20 represents a structural diagram of the cast alloys. The amount of copper in the primary solid solution is shown as 0.125 per cent. This value may be lowered in annealed alloys.

Other cadmium alloys were made and examined for one of three reasons: to determine the effect of additions of other metals to the cadmium-silver-copper series; to determine the possibilities of adding other metals such as antimony, nickel or zinc to the cadmium-silver alloys in place of copper; to make comparative checks of other binary cadmium alloys such as cadmium-nickel, cadmium-magnesium, and cadmium-zinc and the effects of additions to these binary systems. These may be discussed rather briefly:

1—Of the metals added to the cadmium-silver-copper alloys, small amounts of zinc or nickel were found to exert little detrimental

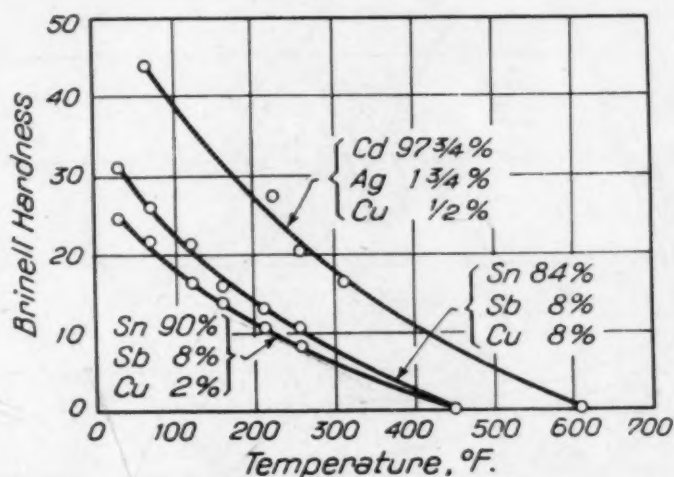


Fig. 18—Brinell Hardness of Cadmium-Silver-Copper Alloys and Tin-Base Babbitts at Elevated Temperatures.

effect on toughness, if the nickel did not exceed 0.25 per cent, or the zinc exceed 0.50 per cent. With greater percentages of either of these present the alloys were undesirably brittle. Extremely small amounts of tin resulted in very brittle castings. Alloys with as little as 0.05 per cent of tin fractured with practically no bend, and exhibited a crystalline fracture. Lead in amounts under 5 per cent imparted brittleness; an alloy with 10.8 per cent of lead showed fairly good ductility, but was softer than was expected. Micro-examination of this sample showed that the presence of any quantity of lead resulted in decreased solubility of silver in cadmium in the primary solid solution. The use of lithium was considered as a possible deoxidizer. The presence of very small amounts of lithium, however, resulted in excessive brittleness.

2—Antimony, in appreciable quantities, added to cadmium-silver alloys imparted undue brittleness. Nickel up to 0.50 per cent im-

proved the hardness of the cadmium-silver alloys without serious effect on ductility. It is considered, therefore, that nickel could replace copper in the ternary alloy, but to no particular advantage.

3—Alloys of cadmium with nickel were decidedly more brittle for a given hardness than the cadmium-silver-copper alloys. Anneal-

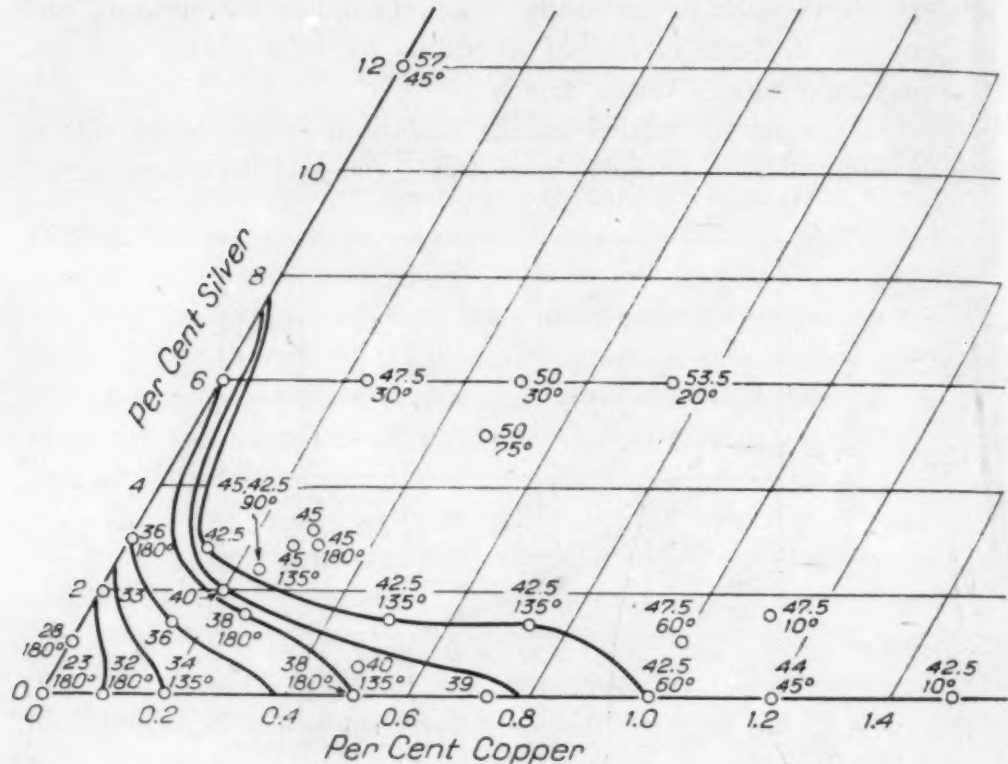


Fig. 19—Hardness Curves for Cadmium-Silver-Copper Alloys.

ing resulted in softening and some coalescence of cadmium-nickel compound, but did not remove brittleness. Cadmium-nickel alloys have been suggested for bearings and their physical properties described by Swartz and Phillips (8). Bearings made of cadmium alloy containing approximately 1.25 per cent nickel have been in use in large production for some time with reported good performance.

Cadmium-zinc alloys of approximately eutectic composition (17.5 per cent zinc), and higher in zinc, showed a high degree of sensitivity to cooling conditions, cold working, or annealing. The rapidly cooled alloys were hard and quite brittle. Annealing or cold working resulted in a very decided softening.

Zinc forms a eutectic with cadmium at a composition shown as 17 and 17.5 per cent of zinc, the melting point of the eutectic being given as 505 to 508 degrees Fahr. Zinc also appears to be somewhat

soluble in cadmium in the alloys as cast, but precipitated from solution almost completely on annealing. Jenkins (9) gives data for cast cadmium-zinc alloys which show an increase in tensile strength and Brinell hardness up to the eutectic composition and a considerable decrease in hardness resulting from annealing. The ductility of the cast alloys was very low at 5 and 6 per cent of zinc, and con-

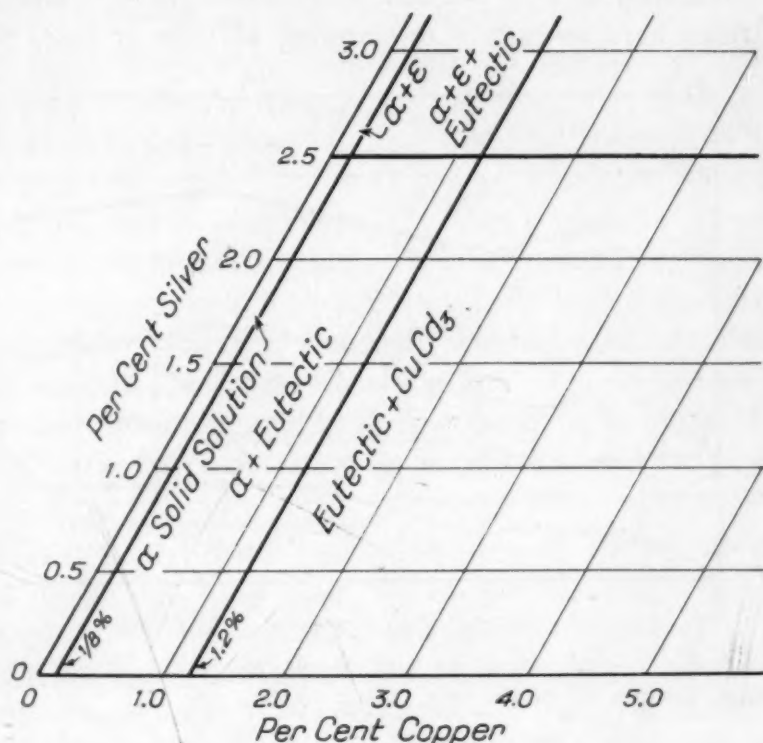


Fig. 20—Cadmium-Silver-Copper Structural Diagram.

siderably better at higher concentrations. Data are plotted in Fig. 21.

Relatively high zinc alloys with additions of some silver were decidedly poor in ductility. It was noted that in the presence of 12.5 per cent of zinc, the solubility of silver in cadmium was markedly decreased.

Engine tests made on connecting rod bearings cast from an alloy of 1 per cent silver, 0.25 per cent copper, 20-21 per cent zinc, balance cadmium, were unsuccessful, resulting in scored shafts in only short mileages.

The addition of 0.4 per cent mercury to an alloy of 0.125 per cent copper did not show any appreciable change. Likewise, the addition of 1.6 per cent of mercury to the 2.5 per cent silver, 0.25 per cent copper alloy had little, if any, effect on hardness or ductility.

Cadmium-magnesium alloys showed some good physical properties, but were very sensitive to conditions of treatment. An alloy of 0.10 per cent magnesium was very tough as cast; annealed and slowly cooled from 550 degrees Fahr., the ductility remained good and some softening occurred; annealed at this temperature and water quenched, the alloy was softened; but extremely brittle with a coarse fracture. An alloy of 0.38 per cent magnesium was extremely brittle and 54 Brinell hard as cast. On standing 45 days at room tempera-

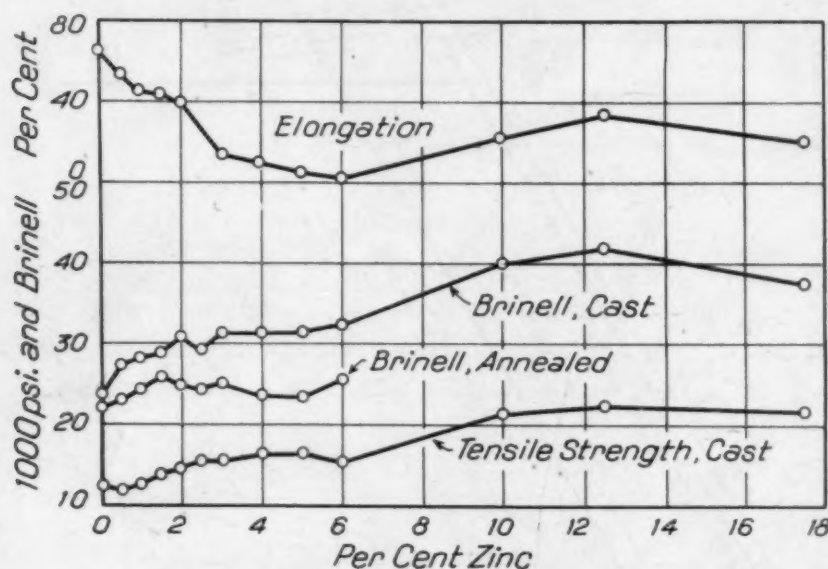


Fig. 21—Physical Properties of Cadmium-Zinc Alloys (Jenkins, *Journal, Institute of Metals*, 1926, Vol. XXXVI).

ture, the alloy was still brittle, but the hardness had dropped to 45 Brinell. An alloy of approximately 2.7 per cent magnesium as cast checked 58 Brinell hard and took a 90-degree cold bend before fracture; after standing 35 days at room temperature, the hardness had dropped to 50 Brinell and the specimen was brittle; heated to 575 degrees Fahr. and water-quenched, the hardness value rose to 60.5 Brinell; cold hammered to 50 per cent reduction the hardness dropped to 32.5 Brinell. An alloy of slightly over 5 per cent magnesium checked 50 Brinell and brittle as cast; heated to 575 degrees Fahr. and water-quenched, the hardness was 64.5 Brinell and a cold bend of 90 degrees was required for fracture. An alloy of 0.10 per cent magnesium and 0.125 per cent copper checked 36-38 Brinell as cast; and 23 Brinell after annealing 16 days at 210 degrees Fahr.

Such results indicate a transformation in the solid state for cadmium-magnesium alloys with relatively small percentages of magnesi-

um. This is indicated for higher magnesium contents in some of the structural diagrams published and indicated for low magnesium content in the diagram by Grube (5). (See also Hume, Rothery and Rowell) (10). The latter state that all alloys up to 6.5 per cent magnesium consist of a single solid solution, with no transformation in the solid state, and will not suffer if kept above room temperature. Our results do not agree with theirs.

The alloy 96.7 per cent cadmium, 3.1 per cent copper, 0.2 per cent magnesium has been suggested as a suitable bearing metal by Accleshaw (11). Hardness of this alloy is reported as 48 Brinell with melting point of 320 degrees Cent. (610 degrees Fahr.).

The alloys of cadmium-silver-copper possess characteristics which appear highly desirable for bearing metals, i.e., low frictional properties, high strength and toughness, relatively high melting point, good temperature stability, freedom from low melting point constituents, a wide range of hardness possibilities without too much sacrifice of toughness, no undue casting or machining difficulties. The selection of a particular composition is, of course, subject to operating requirements.

According to the author's conception of the mechanics of the progress of fatigue failure in engine bearings, the structure of the bearing alloy, and not hardness alone, is of vital importance. Based on the weakest link in the chain line of reasoning, it would seem logical to assume that the weakest component of a bearing metal would largely determine its fatigue resistance. This, naturally, is subject to some modification by the keying action of properly distributed and properly proportioned hardening and strengthening crystals. Thus, in an alloy of more than one structural component, the component of lowest melting point, or lowest strength at operating temperature would be expected to predominate in affecting fatigue life, provided that this component was present to any degree in continuous phase. If this is the case, then, for best fatigue life, the weakest component should be selected with a view to making it the best possible of the compositions available. In alloys consisting mainly of a solid solution primary crystal, reinforced by a secondary constituent of compound, eutectic, or second solution, the composition of the primary crystal should offer maximum strength. Hardness alone, therefore, would not be a criterion of fatigue resistance, and particularly in bearings subjected to edge loading by reason of shaft deflections, hardness which is accompanied by brittleness may be undesirable.

The alloys of cadmium-silver-copper offer a considerable range for the choice of physical properties to fit a particular bearing requirement. The optimum would appear, for best bearing fatigue life, to place the silver content close to the upper limit of the primary solid solution, and to add to this the maximum of copper which would impart hardening and strengthening without excessive brittleness, both silver and copper contents to be consistent with variations to be expected in commercial practices. Accordingly, the selected composition was cadmium 97.5 per cent, silver 2.25 per cent, copper 0.25 per cent. The requirements of bearing metals being as they are, experience may suggest variation from this composition where such items as cost, greater plasticity, higher dirt absorbing ability, etc. may be considered to be the main features. An alloy of 0.75 per cent silver, 0.50 per cent copper is recommended by one bearing maker.

Losana and Gorla (12) studied cadmium-silver-copper alloys by means of cooling curves and micro-examination. They state that the best antifriction alloys are in the region of 0.2 to 0.3 per cent silver and 1.3 to 1.8 per cent copper.

The adaptation of cadmium-silver-copper alloys to bearings necessitated the determination of suitable conditions for melting, fluxing, casting and bonding the alloy to the backing metal.

The conditions for melting and casting are complicated only by the tendency to oxidize at high temperatures unless protected by a suitable flux. The alloy melts at 610 degrees Fahr. and is sufficiently fluid to cast well into centrifugal or continuous strip castings at temperatures around 750 degrees Fahr. Zinc chloride (melting point 504 degrees Fahr.) makes a reasonably good protective covering to prevent surface oxidation. Stirring the melt occasionally with a pine stick deoxidizes and improves the ductility of the metal. (The following flux is mentioned by Hume, Rothery and Rowell (10) as a covering for cadmium alloys—896 parts anhydrous magnesium-chloride, 320 parts potassium-chloride, 40 parts calcium-fluoride, 60 parts sodium-chloride).

Tests of several alloys were made to determine a suitable bonding alloy. The cadmium-silver-copper alloys do not bond directly to steel and, accordingly, it was necessary to find a metal which would perform this function. The cadmium-zinc alloys of approximately eutectic composition, the cadmium-nickel alloys, or the alloys of cadmium-zinc-nickel, of about 5 per cent zinc and 1 per cent nickel, all give excellent bond strength.

The use of these adds small percentages of zinc or nickel to the finished bearing metal. As pointed out previously, this is permissible if held to a low value.

The conditions for bonding are relatively simple; the steel must be scrupulously clean and free from grease, oxides, etc. It must be fluxed with a suitable flux such as zinc-chloride and hydrochloric acid, in water, the time and temperature for immersion in the bonding bath must provide adequate opportunity for "tinning," and finally, casting should follow immediately to avoid chilling below the diffusion and bonding point.

A discussion of the factors affecting bond, and methods of testing for strength and toughness of bond, is not within the scope of this paper. It should be emphasized, however, that good bond strength at operating temperature is a very important factor in bearing life.

Test bars, bonded with cadmium-zinc bonding alloy and joined together by casting bearing metal between the ends, showed considerably higher bond strength than bars similarly made up with tin and babbitt.

While the cadmium-silver-copper alloys do not appear to be affected as greatly by cooling rate as do the tin-base babbitts, nevertheless a rapid rate of cooling after casting is desirable for fineness of grain and maximum hardness and toughness combined. Steel backed bearings made with this alloy may be flattened out and bent double, with the bearing metal surface outside, without cracking the bearing alloy or tearing it loose at the bond face.

In general, these alloys were found to fit quite well into all the practices developed for making babbitt bearings—the temperature employed, the casting properties for either centrifugal or strip casting, the forming and machining properties all meeting the requirements of existing production plants with but slight modification from practices established for babbitt.

Bearings made from cadmium-silver-copper alloys were compared with babbitt bearings over many miles of actual car performance under the most severe operating conditions. The averages of these results indicated that the fatigue life of the cadmium-silver-copper bearings was approximately three times that of the best available babbitt bearings. While slightly greater clearance developed than was the case with babbitt bearings, this was not excessive and the resistance to wear and the freedom from tendency to wear the shafts

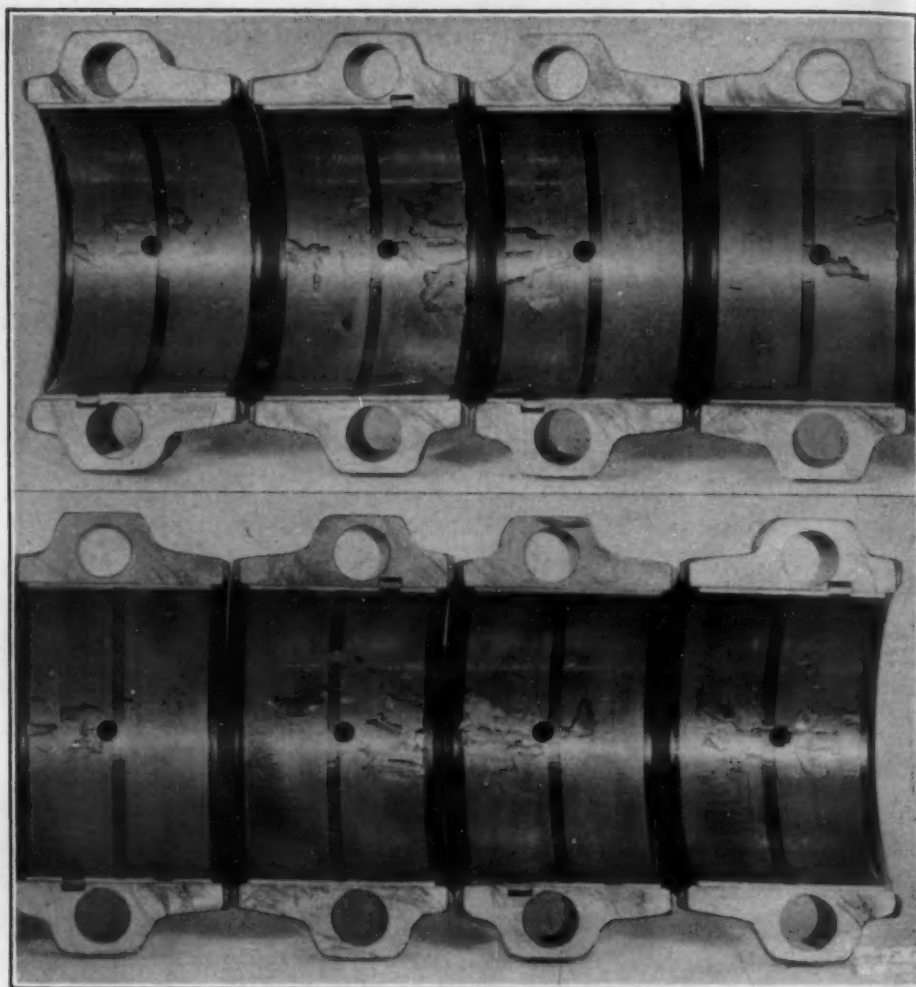


Fig. 22—Photograph Illustrating a Typical Fatigue Failure of Babbitt Bearings Run in an Automobile Engine.

was commendable. The plasticity of this metal proved to be sufficient to permit bearings to accommodate shaft deflections without danger of scoring or seizure, and the toughness was adequate to avoid cracking out at the edges of the bearings. The fitting clearance between shaft and bearings, important where, as is the case with passenger car engines, the noise level should be held to a minimum, could safely be held to as low a value as with babbitt.

Photographs of bearings from actual car service illustrate the comparative excellence of the cadmium-silver-copper bearings. Fig. 22 is a photograph illustrating a typical fatigue failure of babbitt bearings, while Fig. 23 is a photograph of the cadmium alloy bearings after approximately three times the mileage under the same conditions of operation.

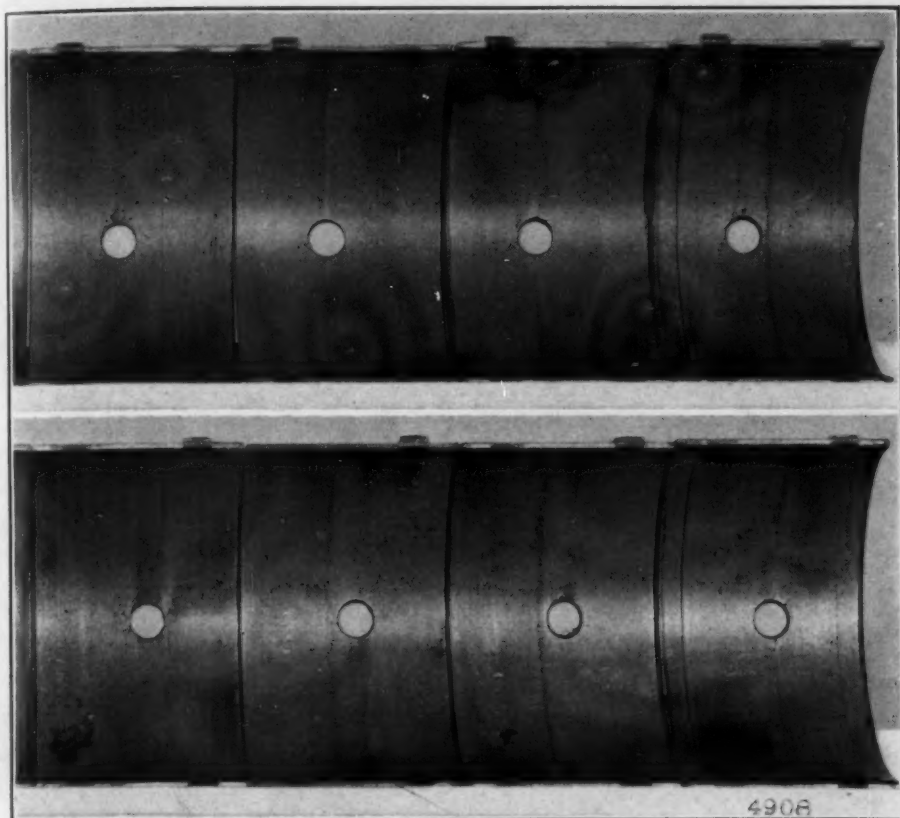


Fig. 23—Photograph of the Cadmium-Silver-Copper Alloy Bearings Run Approximately Three Times as Long as the Bearings Shown in Fig. 22.

Bearings of this type are subject to two objections. First is the commercial situation with regard to the supply and cost of cadmium. The cost of the metal, stabilized at 55 cents per pound for several years, rose to over \$1.00 per pound when the demand for cadmium for automobile engine bearings reached an appreciable quantity in relation to the available supply. This situation will, in all probability, be affected by several factors—the development of additional cadmium recovery equipment, the increasing use of zinc instead of cadmium for numerous plating operations, and the possible more economical application of the metal in bearings as thinner layers are proven acceptable. These should tend to bring about an equitable relationship of price to use.

Second is the developed fact that cadmium alloys, along with some other materials of engine construction, are susceptible to corrosive attack by organic acidic compounds in lubricants. These may either be added, as is the case with certain compounded lubricants, or may be developed in some petroleum oils under the conditions of

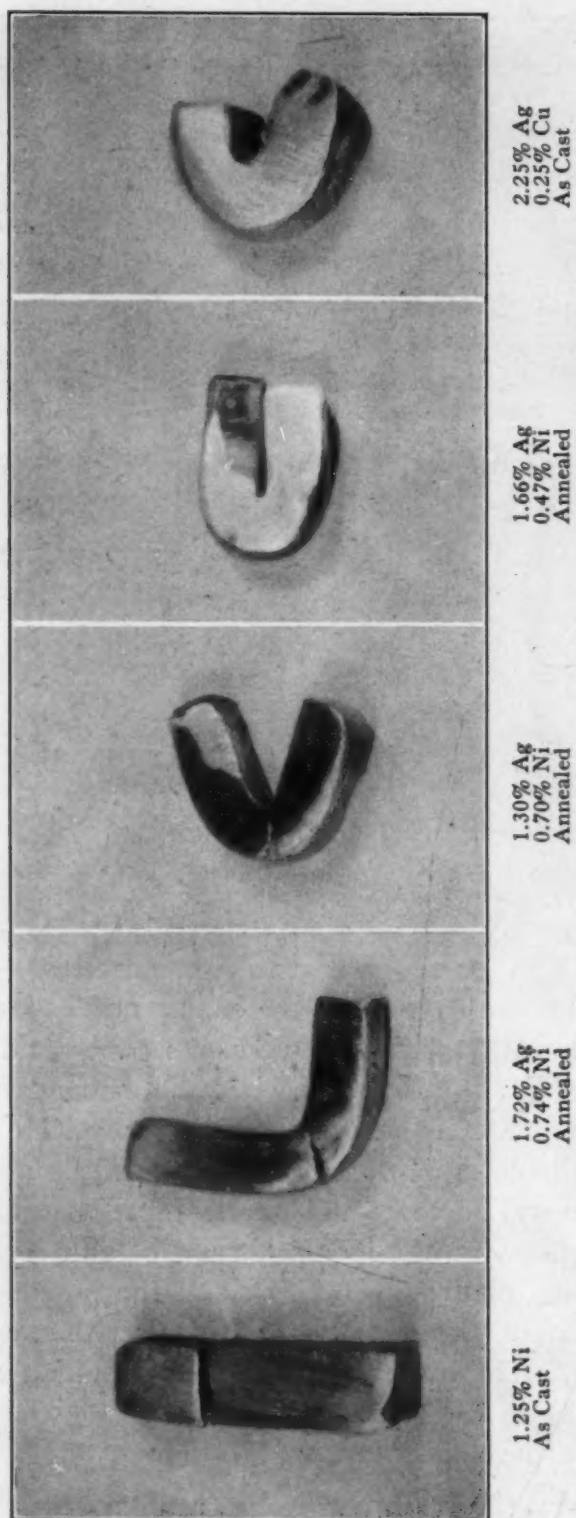


Fig. 24—Cold Bend Test Specimens. Composition and Physical State Listed Under Each Specimen.

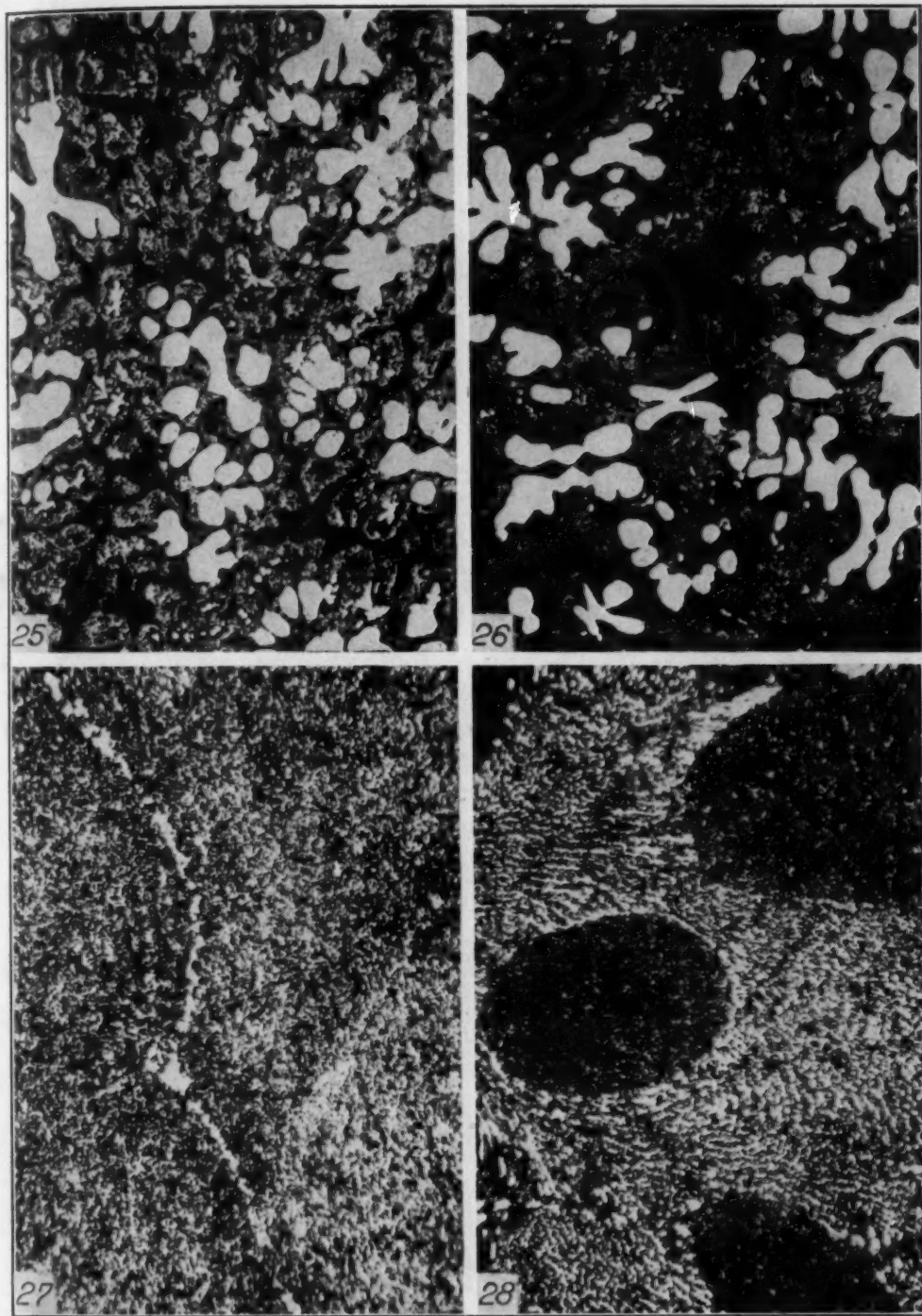


Fig. 25—Alloy 2-6. 6.00 Per Cent Silver. As Cast. Iodine Etch. $\times 100$. Primary Solid Solution of Silver in Cadmium (Cored Matrix) and Second Solid Solution of Silver in Cadmium (White Masses).

Fig. 26—Alloy 2-6. Annealed at 575 Degrees Fahr. $1\frac{1}{2}$ Hours. Iodine Etch. $\times 100$. Second Solid Solution Not Absorbed by Annealing Treatment.

Fig. 27—Alloy 3-2. 0.125 Per Cent Copper. As Cast. Iodine Etch. $\times 500$. Solid Solution Matrix with Trace of Eutectic in Grain Boundaries.

Fig. 28—Alloy 3-6. 1.00 Per Cent Copper. As Cast. Iodine Etch. $\times 500$. Solid Solution Plus Eutectic.

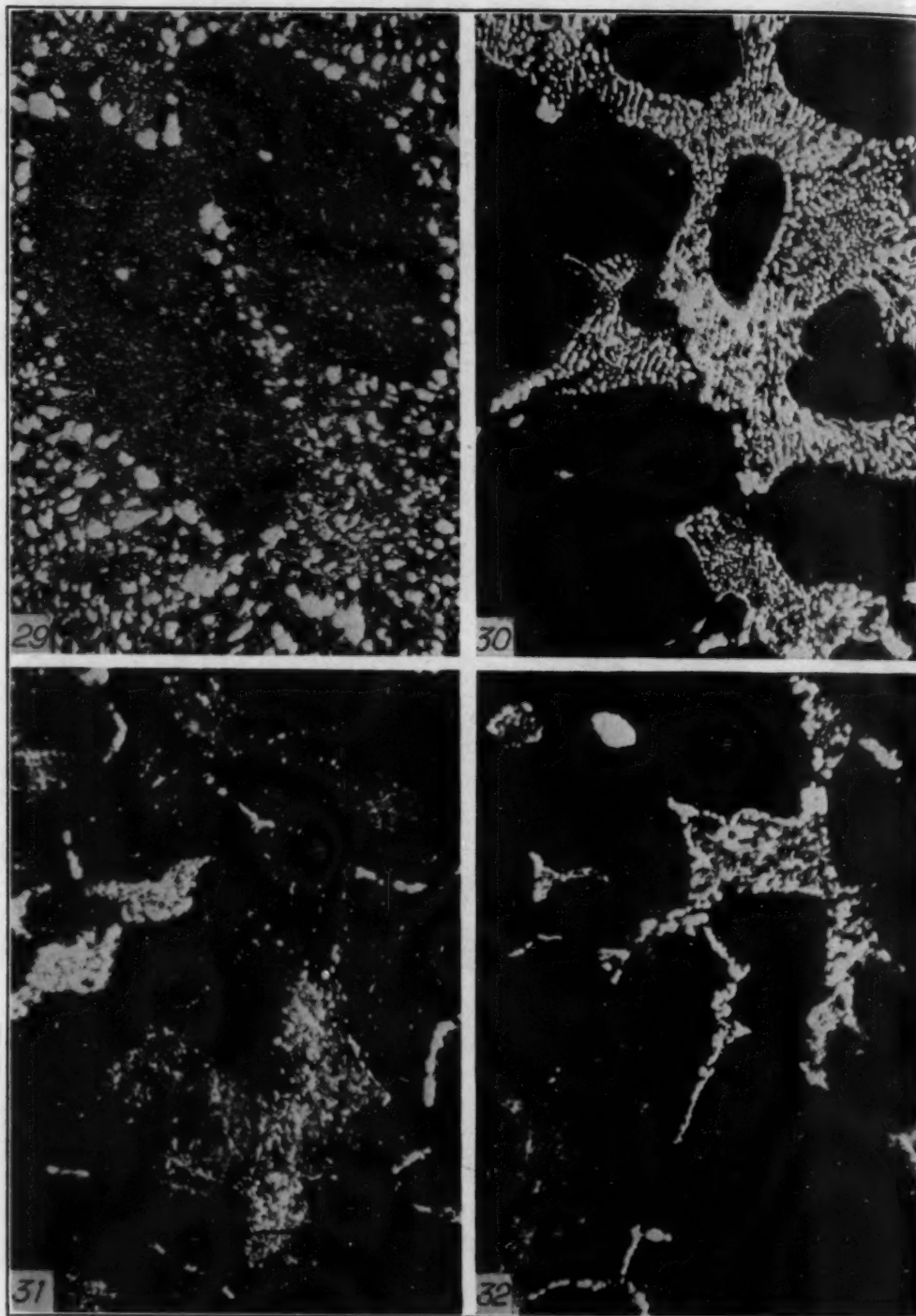


Fig. 29—Alloy 3-6. Annealed 3 Hours at 575 Degrees Fahr. Iodine Etch. $\times 500$. Cadmium-Copper Compound Coalesced by Heat Treatment.

Fig. 30—Alloy 4-4. 1.25 Per Cent Silver, 0.75 Per Cent Copper. As Cast. Iodine Etch. $\times 500$. Primary Solid Solution Plus Eutectic.

Fig. 31—Alloy 4-14. 2.52 Per Cent Silver, 0.26 Per Cent Copper. As Cast. Iodine Etch. $\times 500$. Primary Solid Solution Plus Eutectic.

Fig. 32—Alloy 4-18. 2.82 Per Cent Silver, 0.31 Per Cent Copper. As Cast. Iodine Etch. $\times 500$. Primary Solid Soution, Second Solid Solution and Eutectic.

engine operation. The former (harmful addition agents) should be intelligently refrained from. The latter has been the subject of much study since the fact of its occurrence has been made apparent. Some excellent co-operative work between the petroleum and automotive organizations has resulted in a clear understanding of the factors involved and practical methods have been developed for treating of lubricants to overcome this tendency to oxidation and formation of acidic components.

A good deal of work has also been done in attempting to improve the resistance of the cadmium alloys to corrosion by these organic acids. It is possible, at this time, to report very promising progress in this regard, and it is hoped that at some early future date the details of this work may be presented.

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DISCUSSION

Written Discussion: By Carl E. Swartz, chief metallurgist, Cleveland Graphite Bronze Co., Cleveland.

Mr. Smart is to be commended on the splendid work which he has done in developing the cadmium-silver-copper bearing alloy. Aside from the objections discussed in the latter part of his paper, it is generally agreed that this alloy has given an excellent account of itself in automotive bearings.

Sufficient work has not been done on this ternary alloy to establish the exact limits of the various phases and identify the constituents developed. It seems quite certain, however, that Mr. Smart is pioneering a new type of bearing alloy. Until the advent of this alloy many, if not all, metallurgists interested in bearings were of the opinion that a successful bearing must be composed, not only of a polyphase alloy, but one in which the phases differed

markedly in physical properties. The classical alloy structure in the one hundred years since Sir Isaac Babbitt's time has been that of a relatively soft ductile matrix with one or more relatively hard phases embedded in it.

Mr. Smart's recommended alloy of 2.25 per cent silver, 0.25 per cent copper with cadmium is in all probability not of this type. The second phase, if present, is present in minor amounts; and in hardness does not seem to be far different from the major phase, certainly not as different as the phases of other commonly used bearing materials.

Therefore, I believe metallurgists should congratulate Mr. Smart for his courage in pioneering a bearing alloy which was an exception to the commonly accepted theory of bearing metallurgy.

Written Discussion: By Albert J. Phillips, research department, American Smelting and Refining Co., Maurer, N. J.

Mr. Smart gives, in his paper, the properties of some cadmium-nickel alloys and remarks on page 592 that cadmium-nickel alloys were decidedly more brittle for a given hardness than cadmium-silver-copper alloys, and further states that annealing did not remove brittleness. His statements would imply from the data in his Table I, that cadmium-nickel is too brittle for satisfactory performance as a bearing. I should like to correct this impression:

A cadmium-nickel alloy containing 1.35 per cent nickel, at room temperature has a tensile strength of 16,400 pounds per square inch, elongation of 19 per cent, and reduction of area of 43 per cent. As the temperature increases, the ductility of the alloy increases markedly for at 200 degrees Cent. (390 degrees Fahr.) the elongation is 116 per cent and the reduction of area, 76 per cent. These values would readily indicate that the alloy, as commercially used, is far from brittle. However, to check Mr. Smart's bend tests, I have had cast up samples of a cadmium-nickel alloy containing 1.35 per cent nickel, and the cadmium-silver alloy recommended by Mr. Smart, containing 2.25 per cent silver and 0.25 per cent copper. In addition, I have prepared similar samples of tin babbitt containing 5.23 per cent copper and 6.2 per cent antimony. Our bend tests showed that the cadmium-silver alloy did bend more than cadmium-nickel but we did not get bends of 180 degrees; the bends varied from 40 to 55 degrees. However, our cadmium-nickel samples bent from a minimum of 35 to a maximum of 45 degrees, whereas straight tin babbitt bent only from 20 to 30 degrees.

I believe these tests indicate fairly well the relative order of ductility of the alloys. It is my contention that the cadmium-nickel bearing alloy is less brittle than ordinary tin babbitt, and consequently is amply ductile for all practical service. That the alloy is ductile is demonstrated by the fact that it can be readily fabricated into bearings by the flat strip process. Mr. Smart, of course, realizes that cold bend tests and hardness tests certainly are not sufficient to indicate alloys for bearing purposes. For example: The Brinell hardness and bend values obtained for his cadmium-silver-copper alloy can be very nicely duplicated by a great many copper-zinc and other copper base alloys. I think it is generally agreed that such alloys are not satisfactory for bearing metals. The best criterion for good bearing metal is still actual service test, and Mr. Smart shows in Figs. 22 and 23 that the cadmium-silver-copper alloy is undoubtedly superior to the straight tin babbitts under severe service conditions

and he is to be congratulated for his work in developing an improved bearing alloy that will meet the severe demands of even the most modern automobile engine.

Written Discussion: By Oscar E. Harder, assistant director, Battelle Memorial Institute, Columbus, Ohio.

This paper by Mr. Smart is both interesting and timely. Battelle Memorial Institute, since the beginning of technical activities in 1929, has been interested in cadmium-base alloys, much of the work being for the Federal-Mogul Corporation. Our findings are in good general agreement with the results reported by Mr. Smart.

The author, on page 574, points out that cadmium offered promise as a bearing-alloy base because of the known low frictional effect between cadmium and steel. I should like to add to this by pointing out that silver, which is depended upon almost entirely to modify the matrix of these alloys, a solid solution of silver in cadmium, is a metal which has extremely low affinity for iron and steel; in fact, silver can be melted in iron containers without being contaminated with the iron. The low, or lack of, affinity of silver for iron, it seems to me, may be of very important significance with reference to the good performance of the cadmium-silver-copper alloys for bearings when working against steel surfaces. Excellent bearings have been made of silver-cadmium alloys, and Mr. Smart's paper indicates that when the silver is not present in the cadmium-base alloys the performance as bearings is less satisfactory.

I am glad to note that the author has pointed out the error in earlier literature with reference to the maximum solubility of silver in cadmium. The solubility of silver in cadmium depends somewhat upon the method of preparing the alloys, particularly on the rate of solidification and cooling, and is probably even lower than 2.5 per cent as noted by the author.

The author's diagram for cadmium-silver-copper alloys (Fig. 20) may require revision with further study, because it indicates that neither silver nor copper affect the solubility of the other in cadmium, but the general picture is undoubtedly about as indicated.

As an item of industrial interest, Frank J. Oliver, writing in *Iron Age*, September 17, 1936, page 67, states that in order for the Federal-Mogul Corporation to produce \$20,000 worth of cadmium-silver bearings daily the plant must have in process \$80,000 worth of the cadmium-silver alloy. While these bearings are generally referred to in the trade as cadmium-silver alloy, they also contain copper. The use of cadmium-base alloys for bearings decidedly upset the equilibrium of the cadmium market and caused a marked increase in the price of cadmium. However, existing plants are now producing more cadmium, and additional plants are producing the metal this year.

The lubrication problem is interesting, and without going into detail it appears that the manufacturers of lubricants found that just when they thought they had about attained the last word in refining their products that they had thereby increased the corrosion attack on certain metals. This, of course, suggests that some corrosion-inhibiting agent had been removed. This situation was quickly recognized, and manufacturers of lubricants have been announcing lubricants which have been treated to eliminate this trouble, which at its worst had been quite limited in occurrence. Thus, with some improvement in the

cadmium metal situation and prospects of elimination of the limited corrosion difficulties, the future for the cadmium-silver-copper alloy bearings looks attractive, and further reports from Mr. Smart will be anticipated with much interest.

Written Discussion: By Clair Upthegrove, department of metallurgy, University of Michigan, Ann Arbor, Michigan.

A paper on the subject of bearing metals is always of interest, and particularly so, when it deals with the newer alloys. The author presents the results of a large amount of experimental work and along with them a very clear statement of the reasons for a bearing metal.

The relationships shown in Figs. 14 and 15 between cold bend and hardness properties are of interest in that if the break in the bend curve of Fig. 15 at 0.2 per cent copper be ignored, then the bend properties of both the cadmium-copper and the cadmium-silver alloys are independent of hardness up to certain limiting points. Beyond that point the bend properties fall off rapidly. This decrease would seem to be more a function of the structure than the hardness. Can the author state whether or not similar relationships may be expected at higher temperatures for the hardness and the bend properties?

It is observed in connection with several of the severely cold hammered or worked specimens that the Brinell hardness showed no appreciable increase over the original hardness, that is before hammering. Were any precautions taken to prevent heating of the metal as a result of the hammering operation?

In speaking of the effect of the annealing of the cadmium-copper alloys, it is stated that the annealing also caused a complete precipitation of the copper-cadmium compound which appeared to be held in solution in the rapidly cooled casting. Might it not be more probable that the softening observed is instead the result of the resolution rather than the result of the precipitation and coalescence of the compound? This would also account for the increase in ductility.

In connection with the work of Losana and Gorla, it should be pointed out that they also suggested along with the 0.2 to 0.3 per cent silver and 1.3 to 1.8 per cent copper alloys the use of alloys of 1.0 to 2.0 per cent silver and about 0.2 per cent copper, a composition range very similar to that recommended in the present paper.

Written Discussion: By E. R. Darby, director of research, Federal-Mogul Corp., Detroit.

Having been actively engaged in the study of cadmium-base bearing alloys for a number of years, I am of course much interested in this excellent paper by Mr. Smart. He has so thoroughly covered the important characteristics of these alloys that there is little to offer of an additive nature.

Although work-softening is an old story, it may be of interest to those whose activities have been directed in other lines to point out here the effect of cold deformation on the soft metals and alloys used in bearing linings. Usually, with respect to engineering materials, cold deformation or work is thought of as a means to improve the desirable properties, strength, and hardness. Heating such deformed material results in softening. With respect to lead, tin, and cadmium and many of their alloys, such characteristics do not obtain. Instead, cold deformation, at least of a critical nature, is accompanied by softening and subsequent heating results in a recovery of at least a portion

of the hardness of the metal as cast. An excellent example may be found in Britannia Metal. As cast, this alloy has a hardness close to 24 Brinell. When severely cold-rolled, its hardness may drop as low as 15 Brinell. Heated for a short while at 400 degrees Fahr. (205 degrees Cent.), a remarkable recovery is noticeable and the hardness will rise to a value but slightly below that of the cast alloy. Cadmium and the cadmium-rich cadmium-zinc alloys have the same characteristics, and Mr. Smart shows in Table I that the cadmium-silver-copper compositions perform in a similar manner.

This softening effect of cold work is not of very great importance from a bearing standpoint, but certain other phenomena of similar effect are of moment. The data in Table I of Mr. Smart's paper indicate that certain alloys of cadmium-silver-copper are greatly reduced in hardness by a low temperature anneal. We have found in our work with these compositions that this loss in hardness may be, to a large extent, regained by subsequent anneal at higher temperatures. An alloy of silver 0.75 per cent, copper 0.05 per cent, cadmium—remainder has a cast hardness of from 39 to 41 Brinell. Upon heating a specimen of the cast alloy at 212 degrees Fahr. for a few hours, the hardness is reduced to 30-33 Brinell. If the specimen be then reheated to a higher temperature, 400-450 degrees Fahr. (205-235 degrees Cent.), most of the cast hardness will be recovered and values from 35 to 38 Brinell have been recorded.

Mr. Smart explains the softening of the cadmium-copper compositions, when heated to 210 degrees Fahr., by assuming a more or less complete precipitation of the copper held in solution in the chilled alloy; in other words, precipitation softening and solution hardening. I am inclined to agree with this explanation, only in our work it appears that the upper limit of solubility is much lower than 0.125 per cent, possibly as low as 0.03 per cent.

Although this softening of the cadmium-silver-copper alloys is of technical interest, I am of the opinion it is also of practical importance, as in the early stages of engine operation the softening facilitates adjustment in bearing surface contour. A Brinell hardness of 40 is fairly high for the average engine crankshaft, but in service these alloys will have this hardness so rapidly relieved that they really perform as a softer material.

Author's Closure

It has been very interesting and gratifying to have these discussions and I wish to express my thanks to these gentlemen for their contributions to this subject.

In reply to Professor Upthegrove's inquiries, I would state (1) that the ductility of the cadmium-silver and cadmium-copper alloys, as indicated by the bend test, was better at elevated temperature (400 degrees Fahr.) than at room temperature, where the latter was less than 180 degrees bend; (2) that no special precautions were taken to prevent heating of the alloys during hammering and that the temperature of the hammered specimens was undoubtedly raised although no attempt was made to measure this; (3) that coalescence of the copper compound does occur to a very marked degree—my inferences as to copper solubility were based on the inability to resolve the structure of alloys up to 0.125 per cent copper at 500 magnification and the difference in slope of the hardness curve for alloys below and above this point.

The information presented by Dr. Harder and Mr. Darby is of particular interest because they have been working with similar alloys, and I am pleased to note their general confirmation of my data.

Dr. Swartz mentions the long held theory of the necessity of a duplex structure for successful bearing metals. This, I believe, has been questioned more frequently in recent years. Very good service results have been obtained with a babbitt of 2.25 per cent copper, 8 per cent antimony, rapidly cooled to suppress the formation of tin-antimony cubes and coarse tin-copper crystals. Bearings of pure tin and pure cadmium have been run experimentally with fair results. Our extended use of electro-deposited tin as a bearing surface on engine pistons has been very successful in service. Such data have indicated that some pure metals or alloys without definite hard and soft phases offer good bearing properties.

Mr. Phillips states that he could not obtain bend tests on the cadmium-silver-copper alloys such as I have reported. Evidently there is some difference in our procedure. I have checked my results a number of times, both on the alloy as used for experimental bearings and on metal used for production bearings. A photograph (Fig. 24) illustrates the degree of bend obtained on an alloy of cadmium with 1.25 per cent nickel and one of cadmium with 2.25 per cent silver, 0.25 per cent copper, both as chill cast, also the alloys of cadmium with 1.72 per cent silver, 0.74 per cent nickel; 1.30 per cent silver, 0.70 per cent nickel; and 1.66 per cent silver, 0.47 per cent nickel as cast and annealed. (These latter alloys, made and examined since the presentation of the paper, appear of considerable interest).

It has been the author's experience with automotive engine bearings that the high copper, high antimony relatively brittle babbitts did not give as good service life as a much tougher lower copper babbitt, and it is because of this experience that we have felt that relative brittleness was an important factor in bearing materials.

I would not wish to be understood as suggesting that bend test values and hardness test values of themselves are sufficient criteria by which to judge the suitability of metals for bearing purposes. They may, however, act as guides in the selection of compositions from a family of alloys possessing known basically desirable features. The final test, I wholly agree with Mr. Phillips, must be the performance in service since no known laboratory tests can duplicate all the variables of practice.

THE RETARDING EFFECT OF CERTAIN METALLIC ELEMENTS ON GRAPHITIZATION

BY H. A. SCHWARTZ, H. H. JOHNSON AND C. H. JUNGE.

Abstract

The effects of chromium, manganese, molybdenum and vanadium on the graphitizing reaction are studied from the viewpoint of their effects on the graphite nodule number per unit volume and on the migratory rate of carbon in iron. Data are given for the progress of graphitization with time of strictly comparable alloys differing only in content of the graphitizing retarder. The study is limited to relative low concentrations of the retarders. Data are also given as to the size distribution of the graphite nodules resulting from the graphitizing reaction.

An attempt, probably the first in the literature, is made to correlate the expected, and observed, retardation of graphitizing rate by these elements with the nuclear number and migratory rate. It is found that the addition of manganese increases the number of nuclei capable of growth at 900 degrees Cent. (1650 degrees Fahr.) while additions of the other elements reduce this number. Additions were of little effect on nuclei capable of growth at 700 degrees Cent. (1290 degrees Fahr.).

The migratory rate of carbon in gamma iron was found to be retarded by all the alloying elements while the graphite solubility was not distinctly altered. The retardation is a function of the concentration added and does not differ greatly for the several elements studied.

Chromium greatly retards migration rate below A_1 , the other elements having but little effect. It is likely that the retarding effects of the elements are also functions of the carbon content of the metal. A warning is given that useful data as to the effect of other elements on graphitizing rate can be secured only by comparisons based on material of precisely similar history in the melting operation.

IT is well known that the graphitizing reaction is retarded by the presence of certain elements in abnormal amount.¹ Among these are the metals chromium, manganese, molybdenum, vanadium, which

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have become important as retarders in various commercial processes for making "pearlitic malleable cast iron."²

It has long been recognized that the retarding effect of these elements is not always similar in the two stages of annealing. The fairly voluminous bibliography of these elements deals mainly with measurements of graphitizing time and gives little consideration to the mechanism of retardation. There may be room therefore for observations correlating graphitizing rates, with other significant factors such as carbon solubility, number of nuclei and form of graphite nodules.

Space does not permit a recapitulation of certain matters fundamental to the present subject. The time-graphite relations in graphitization have been quantitatively investigated³ and reconciled with the theory that migratory rates normally determine graphitizing rates. The method for determining the number of nodules (nuclei) per unit volume, originally suggested by Erich Scheil, has also been described.⁴ Certain generalizations as to nucleus number and a method of measuring the sprawliness of temper carbon have also been published elsewhere.⁵

SCOPE OF THE INVESTIGATION

Obviously, no investigation, such as the present, could cover completely the entire possible field. It is necessary for reasons of time and expense to arbitrarily limit oneself to certain restricted areas. For better or for worse the concentration of the retarding metallic elements was kept within the limits which have so far had a commercial interest. Since this range is in all cases fairly small it seemed well to work in each case with only one concentration of the added element although two molybdenum alloys were investigated. To avoid vagaries arising out of melting practice, a companion alloy of the identical metal without additions was studied. In the case of manganese it was thought worth while to include also the effect of

¹Schwartz and Guiler, *Transactions, American Foundrymen's Association*, Vol. 33, 1925, p. 639.

²Symposium on Pearlitic Malleable Iron, Cleveland District Committee, A.S.T.M. in press.

³H. A. Schwartz, "Graphitization at Constant Temperature," *TRANSACTIONS, American Society for Steel Treating*, Vol. 10, 1926, p. 53.

⁴H. A. Schwartz, "The Metallographic Determination of the Size Distribution of Temper Carbon Nodules," *Metals and Alloys*, Vol. 5, 1934, p. 139.

⁵H. A. Schwartz and Wolfram Ruff, "Origin and Growth of Graphite Nuclei in Solid and Liquid Iron Solutions," *Metals Technology*, American Institute of Mining and Metallurgical Engineers, Dec. 1935, p. 655.

varying carbon concentration for its possible value in throwing light on the partition coefficient of the alloying element between austenite and carbide. Therefore all the alloys for the study of manganese were of necessity made in the laboratory rocking electric furnace. The alloys of chromium, molybdenum and vanadium were made by ladle additions to metal from a rotating reverberatory furnace. This difference of melting practice may be viewed as an advantage or a disadvantage. It furnishes examples in the investigation of two types of melting which is desirable, but it makes direct comparison between the manganese alloys and the chromium, molybdenum and vanadium alloys impossible. The latter objection is presumably overcome, in part at least, by having unalloyed alloys of both types available for comparison.

In each case the time-graphite curve of the alloy was determined at 900 and 700 degrees Cent. (1290-1650 degrees Fahr.) and especially attention was paid, particularly at the higher temperature, to the equilibrium value of combined carbon as a measure of the effect of the alloy on the solubility of graphite in austenite. At a favorable degree of graphitization the total number of nodules, and their size distribution per unit area was determined and the ratio of the volume of graphite as determined chemically to the volume of the circumscribing spheres calculated as a measure of sprawliness. The number and sprawliness of nuclei have been shown in the references to vary relatively little with time at a given temperature.

EXPERIMENTAL PROCEDURE

The electric furnace heats for the experiment were made in a 350-pound capacity unit of the rocking type from pig iron, steel and ferro alloys of silicon, manganese, phosphorus and sulphur in such proportions as to give the composition desired for the lower manganese value (0.26 per cent). For the two lower carbon heats charcoal pig was used; for the higher, Chateaugay. The phosphorus and sulphur content was adjusted by calculation to 0.10 and 0.05 per cent respectively. After one-half the heat was poured into test specimens an addition of about 0.50 per cent manganese as ferromanganese was made and the other half of the heat then also cast into specimens. The pouring temperature was kept as near 1535 degrees Cent. (2800 degrees Fahr.), measured by an optical pyrometer sighted on the back wall of the furnace and assumed to read "black body" tempera-

ture, as was practicable. The control was, however, none too good, the low carbon heat being poured at 2809 degrees Fahr., the intermediate at 2868 degrees Fahr. and the high carbon at 2773 degrees Fahr. The furnace normally maintains an atmosphere of about 30 per cent or slightly less CO and the balance N_2 . The flue gas compositions were not determined for these particular heats but there is every likelihood that they constituted no exception to this rule. The furnace lining was a high alumina clay. The air furnace heats to which ladle additions of molybdenum, chromium and vanadium were made were melted under commercial conditions in pulverized fuel fired rotary furnaces with a siliceous lining. The melting stock was sprue, coke pig iron and malleable scrap plus coke and ferro alloys. The phosphorus content is customarily about 0.17 per cent in this practice and the sulphur around 0.06 to 0.07 per cent. The pouring temperatures are, in intent, near 2800 degrees Fahr. but owing to the vagaries of measuring, optically, the temperatures of streams of metal there is no certainty with respect to the pouring temperature in individual cases except that special effort was made to keep similar pouring temperatures for the alloyed and unalloyed pairs of each set. The furnace atmosphere is substantially a mixture of N_2 and CO_2 with fractions of 1 per cent each of CO and O_2 and the (undetermined) amount of H_2O corresponding to the hydrogen content of the fuel.

The metal was cast, in green sand molds, into specimens of the form prescribed for tensile specimens in A. S. T. M. specification A47-33, the grip ends $\frac{3}{4}$ inch in diameter being used for the heat treatments. Pairs of specimens, alloyed and unalloyed, were packed into pipe nipples in cast iron borings, several pairs of different metals being usually in one thimble and heated for the required time at 900 or 700 degrees Cent. in a "Hump" furnace, the temperature being controlled from an iron-constantan thermocouple outside the nipples by a recorder controller. This location of the couple is known to minimize temperature fluctuations inside the nipples by responding sooner to temperature changes. The time of exposure to heat was chosen with reference to the observed reaction rates in order to get a reasonably representative distribution of observations. Generally, the time intervals increased roughly in geometric progression. The specimens were air cooled in their containers and cleaned by grinding off about 1 millimeter of surface metal.

Graphite determinations, usually in duplicate, were made on

pieces of metal representing a fairly complete cross section of the specimens without any crushing or machining thus avoiding mechanical loss of graphite. Color carbons, occasionally used for check purposes, were made using Bureau of Standards standard steel samples of appropriate carbon content. This practice may be defensible on the score of sampling difficulties in graphitic materials. No color carbon data are included in the final summaries. Total carbons were also made on representative pieces of metal by solution in copper potassium chloride and combustion in order to avoid mechanical loss of graphite.

The micrographs upon which the nucleus count was based consisted of four fields from one plane for each specimen. The magnification was so chosen that when an image on a 4 x 5 inch plate was enlarged to 11 x 14 inch the images of the largest temper carbon dots were of convenient size for measurement. Usually their (enlarged) diameter was between 1 and 2 centimeters. The magnification was, of course, accurately known in each case as a basis of calculation. It was frequently x35, occasionally x100, and in one case x150. The references should be consulted for the details of these computations and comments on the technique. When possible the nodules were divided into ten sizes although in some cases it was impossible to subdivide so closely and five sizes only were employed. The smallest sized nodules were divided between graphite and sulphides in the proportion indicated by pilot counts at magnifications sufficient to distinguish between these two phases. Only the graphite nodules were recorded in the count.

The experimental procedure is reported in such great detail for, although it is now commonly understood that graphitization rate may in large measure depend upon the number of nodules of temper carbon formed per unit volume, we still have little knowledge as to the factors determining this number. A complete knowledge of experimental conditions is therefore useful to those seeking to interpret such phenomena. The intent of the procedure, throughout, was to insure the greatest possible similarity between the unalloyed and alloyed specimens.

Experimental Data

The experimental procedure having been so clearly described the data can well be submitted without further comment in the form of a series of tables.

Table I
Composition of Material (Per Cent)

Designation	C	Si	Mn	Cr	Mo	V	Melting Method
11	2.64	0.95	0.31	trace	Fuel
12	2.64	0.95	0.31	0.305	Fuel
21	2.45	0.83	0.29	Electric
22	2.42	0.80	0.74	Electric
31	2.16	0.81	0.26	Electric
32	2.15	0.80	0.77	Electric
41	1.63	0.87	0.27	Electric
42	1.63	0.88	0.79	Electric
51	2.38	0.98	0.29	...	none	none	Fuel
52	2.40	0.98	0.29	...	0.27	...	Fuel
53	2.40	0.95	0.32	...	0.65	...	Fuel
54	2.40	0.95	0.32	0.17	Fuel
61	2.31	0.95	0.28	...	none	none	Fuel
62	2.28	0.95	0.28	...	0.23	...	Fuel
63	2.28	0.98	0.29	...	0.45	...	Fuel
64	2.30	0.98	0.29	0.14	Fuel
*71	2.58	0.93	0.36	Fuel
*72	2.58	0.93	0.83	Fuel
*81	2.36	0.97	0.34	Fuel
*82	2.36	0.97	0.71	Fuel

*The data concerning these specimens have been added since the presentation of the paper. The body of the paper has not been altered to include these materials.

Table II
Graphite Formed at 900 Degrees Cent. (1650 Degrees Fahr.) (Per Cent)

Designation	Hours							
	0	1	2	5	10	21½	51½	85
11	0.06	0.16	...	0.63	1.30	1.63	1.67	...
12	0.06	...	0.18	0.28	0.54	1.08	1.31	1.43
	4	8	16	32	64
21	0.06	0.31	0.57	0.54	1.40
22	0.07	0.70	0.97	1.28	1.41
31	0.08	0.15	0.70	1.11	1.15
32	0.06	0.04	0.21	0.70	1.05
41	0.10	0.19	0.35	0.55	0.64
42	0.13	0.48	0.48	0.48	0.61
	4	8	16	29	30½	64	144	370
51	0.59	0.72	1.35	...	1.43	1.42	1.56	1.50
52	0.17	0.25	0.88	...	1.09	1.31	1.47	1.41
53	0.08	0.14	0.33	...	0.57	1.08	1.37	1.38
54	0.10	0.22	0.56	...	0.94	1.00	1.33	1.38
61	0.20	0.68	...	1.45
62	0.13	0.33	...	1.27
63	0.08	0.21	...	1.03
64	0.10	0.32	...	0.96
	112 Hrs.							
71	1.61
72	1.60
81	1.59
82	1.63

ACKNOWLEDGMENTS

We are indebted to Stowell Wasson, Manager of the Indianapolis Works of the National Malleable and Steel Castings Company for the specimens made in fuel-fired furnaces and to Andrew Heinlein of that plant for making them. W. Kenneth Bock of the Research Laboratory assisted most capably in the tedious task of obtaining the size distribution of the graphite nodules.

Table III
Graphite formed at 700 degrees Cent. (1290 degrees Fahr.) (Per Cent)

Designation	Hours									
	0	20	50	100	170	230	305	450	740	3024
11*	0.06	0.06	0.09	0.40	0.98	1.98	2.49	2.49*	2.23	...
12*	0.06	...	0.06	0.10	0.28	0.57	0.72	1.07*	1.35	1.93
21	40	77	159	288	451	800
22	...	0.20	0.73	0.85	1.27	2.33
31	...	0.21	0.81	1.09	1.20	1.70
32	...	0.07	0.07	1.00	1.59	2.04
41	...	0.06	0.06	0.15	0.16	1.01
42	0.10	0.35	0.65	1.11	1.14	1.47
61	0.14	0.17	0.68	0.94	0.89	1.15
62	41½	68	143	287	451	800
63	0.04	0.05	0.15	0.58	1.60	2.23
64	0.04	0.04	0.06	0.26	0.92	2.03
71	0.03	0.05	0.08	0.19	0.48	1.78
72	0.04	0.07	0.39	1.42	1.91	2.13
81	1514 Hrs.	1.48†
82	...	2.19†
...	...	1.00†
...	...	2.33†

*Decarburization begins to be detectable.

*Actually 710 degrees Cent. (1310 degrees Fahr.).

†Actually 715 degrees Cent. (1320 degrees Fahr.).

Table IV
Combined Carbon at 700 degrees Cent. (1290 degrees Fahr.) after holding 73 hours at 905 degrees Cent. (1660 degrees Fahr.) and cooling in 3¼ hours to 700 degrees Cent. (1290 degrees Fahr.)

Designation	Hours							
	1	4	8	16	28	69	165	282
21	0.58	0.47	0.39	0.06
22	0.78	0.54	0.42	0.41	0.19
31	0.53	0.46	...	0.20	0.12
32	0.77	0.55	0.52	0.35	0.29
41	0.50	0.46	0.38	...	0.20	0.06
42	0.69	0.70	0.54	0.44	0.38	0.31

DISCUSSION OF DATA

The data reported fall naturally into two groups, one of unalloyed, the other of alloyed metal and may correspondingly be profitably discussed from two viewpoints. Logically we may first consider the correlation between carbon content, nodule number and graphitizing rate in alloys of generally similar composition but varying origin. Next we may consider our major thesis the effect of alloying elements on the graphitizing rate, nodule number, carbon solubility and so on, all other variables affecting these characteristics having been excluded so far as our knowledge and skill permitted. The reader is reminded that references have been given in support of the hypothesis that graphitizing rate is determined by the time required

Table V
Minima of Combined Carbon

Designation	900 degrees Cent. (1650 degrees Fahr.)		700 degrees Cent. (1290 degrees Fahr.)		900 degrees Cent. followed by 700 degrees Cent.	
	Comb. C	hrs.	Comb. C	hrs.	Comb. C	hrs.
11	0.97	51½	0.02	740
12	1.21*	85	0.42*	3024
21	1.08	64	0.12	800	0.39*	28
22	1.04	64	0.72*	800	0.19	282
31	1.03	64	0.08	800	0.12	28
32	1.06	64	1.15*	800	0.29	282
41	1.00	64	0.16	800	0.20	28
42	0.92	64	0.48*	800	0.31	282
51	0.91	370	0.07	24
52	1.00	370	0.64	24
53	0.98	370	0.85	24
54	1.03*	370	0.54	24
61	-0.01°	800
62	-0.15°	800
63	0.45	800
64	0.16	800
71	0.97	112	1.10*	1514
72	0.98	112	0.39*	1514
81	0.77°	112	1.36*	1514
82	0.73°	112	0.03	1514

*Reaction incomplete.

*Sic.

Table VI
Number, Maximum Diameter and Density of Packing of Graphite Nodules

Designation	At 900 degrees Cent. (1650 degrees Fahr.)				At 700 degrees Cent. (1290 degrees Fahr.)			
	Time hrs.	Number per mm ³	Dia. mm.	Density Per Cent	Time hrs.	Number per mm ³	Dia. mm.	Density Per Cent
11	51½	146	0.263	30	95	148	0.132	87
12	51½	103	0.298	25	3024	360	0.246	58
21	64	34.3	0.307	33	288	4156	0.077	26
22	64	946	0.219	45	288	5494	0.062	33
31	64	999	0.219	33	288	494	0.175	41
32	64	1556	0.193	32	800	205	0.264	53
41	64	839	0.219	29	288	478	0.248	32
42	64	8811	0.083	22	288	719	0.131	32
51	64	66	0.298	25
52	64	248	0.368	21
53	64	13	0.438	23
54	64	37	0.386	76
61	800	35	0.333	41
62	800	22	0.333	43
63	800	31	0.316	38
64	800	47	0.298	36
71	112	116	0.263	0.32	1514	38.3	0.273	0.88
72	112	103	0.263	0.40	1514	21.2	0.318	0.88
81	112	242	0.219	0.22	1514	6.33	0.455	0.81
82	112	172	0.219	0.28	1514	10.5	0.455	0.82

for carbon to migrate from its initial location in cementite to its final location as graphite. Graphitizing rate should, therefore, be a function of the amount of carbon available, the mean migratory distance, the migratory rate at unit carbon gradient and the difference of carbon concentration in metal saturated with respect to graphite and to cementite.

Since the rate of formation of graphite is most rapid when about

Table VII

Size Distribution of Temper Carbon Nodules (at 900 degrees Cent.)
Number per cubic millimeter

Designation	Max.	Diameter								
		0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
		Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.
11	6.4	0.0	11.5	0.0	16.0	0.0	15.0	0.0	97.5	0.0
12	3.3	0.0	8.1	0.0	11.3	0.0	7.9	0.0	72.0	0.0
21	0.5	3.4	4.9	4.9	2.9	3.1	0.7	2.4	6.7	4.8
22	1.1	3.2	5.0	12.3	18.4	8.8	9.1	3.0	15.0	870.0
31	2.7	1.8	8.1	13.1	10.9	12.7	18.4	15.6	29.2	887.0
32	4.3	3.7	8.2	18.3	17.8	10.4	5.6	18.9	54.3	1414.0
41	4.5	-0.7	0.5	9.1	3.4	7.4	8.3	21.6	51.8	733.0
42	37.4	0.0	71.2	0.0	307.0	0.0	1128.0	0.0	7267.0	0.0
51	3.1	0.0	12.8	0.0	9.4	0.0	6.5	0.0	34.3	0.0
52	1.5	0.0	4.0	0.0	6.1	0.0	4.2	0.0	232.0	0.0
53	0.6	0.0	3.7	0.0	2.3	0.0	1.5	0.0	4.7	0.0
54	0.9	0.0	2.4	0.0	2.9	0.0	4.2	0.0	26.4	0.0
71	6.2	...	21.0	...	22.5	...	22.5	...	44.1	...
72	4.6	...	16.0	...	19.0	...	10.8	...	52.4	...
81	4.2	...	20.2	...	40.5	...	57.7	...	118.9	...
82	5.5	...	13.0	...	26.8	...	56.6	...	70.0	...

Table VIII

Size Distribution of Temper Carbon Nodules (at 700 degrees Cent.)
Number per cubic millimeter

Designation	Max.	Diameter								
		0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
		Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.
11	2.2	0.0	9.7	0.0	11.6	0.0	16.1	0.0	108.0	0.0
12	5.8	0.0	2.6	0.0	10.9	0.0	14.8	0.0	307.0	0.0
21	31.6	46.2	97.3	298.0	473.0	339.0	333.0	277.0	758.0	1504.0
22	193.0	0.0	408.0	0.0	851.0	0.0	2855.0	0.0	1187.0	0.0
31	1.3	2.2	4.0	3.7	22.0	40.5	82.6	138.0	160.0	40.4
32	1.0	0.0	1.5	0.0	6.1	0.0	17.7	0.0	179.0	0.0
41	1.2	0.8	6.3	6.3	14.6	13.0	4.5	6.6	14.1	320.0
42	7.5	0.0	35.0	0.0	130.0	0.0	233.0	0.0	314.0	0.0
61	2.8	0.0	7.3	0.0	7.1	0.0	3.8	0.0	13.8	0.0
62	4.6	0.0	4.1	0.0	0.5	0.0	4.8	0.0	8.5	0.0
63	3.5	0.0	6.4	0.0	6.9	0.0	3.6	0.0	10.7	0.0
64	2.6	0.0	12.6	0.0	13.8	0.0	8.0	0.0	10.1	0.0
71	1.1	...	2.6	...	8.6	...	9.5	...	16.4	...
72	2.4	...	2.2	...	4.2	...	4.9	...	7.6	...
81	0.1	...	0.5	...	1.0	...	1.9	...	2.8	...
82	0.5	...	1.0	...	2.2	...	2.8	...	4.1	...

one-half the carbon available for graphitization has been liberated, the time required to reach this condition is considered the most desirable measure of graphitizing rate. This time is computable from observations near the desired point since the form of the graphitization curve for unalloyed metal is empirically known. For the range from 30 to 60 per cent completion the complex empirical time-graphite curves may be replaced with but an insignificant error by the simpler equation,

$$\text{Time} = 0.3 + 0.014x \text{ per cent completion}$$

where the unit of time is the interval required to precipitate the first

Table IX
Time for 50 Per Cent Completion of Graphitization
900 Degrees Cent. (1650 Degrees Fahr.)

Designation	Time (hrs.)	Per Cent Completion	Time for 50 Per Cent
11	5	38.4	6.0
12	10	32.9	13.0
21	16}	39.3}	18.4} mean 28
	32}	37.2}	38.0}
22	8	49.3	8.0
31	16	60.3	14.0
32	32	60.9	28.0
41	16	55.5	15.0
42	4}	20.6}	6.0*}
	8}	76.2}	6.0*}
	16}	76.2}	12.0}
	32}	76.2}	24.0}
51	8	52.2	8.0
52	8}	18.0}	13.0*}
	16}	63.0}	13.0*}
53	30½	40.7	35.0
54	16	47.1	17.0
61	8	51.9	8.0
62	8	26.4	12.0*
63	8	24.3	11.0*
71} Mn	0.47	all	1.81
72}		sig. only	0.78
81} Mn	0.37	all	1.41
82}		sig. only	1.20

*Interpolated from curves "Graphitization at Constant Temperature," H. A. Schwartz, TRANSACTIONS, American Society for Steel Treating, Vol. 10, p. 53, 1926.

Table X
Time for 50 Per Cent Completion of Graphitization
700 Degrees Cent. (1290 Degrees Fahr.)

Designation	Time (hrs.)	Per Cent Completion	Time for 50 Per Cent
11	170	37.1	21
12	450	40.1+	522
21	288}	34.7}	364}
	451}	51.8}	438}
22	288}	45.0}	310}
	451}	49.5}	455}
31	288	46.3	303
32	800	47.0	833
41	159	40.0	185
42	159}	41.7}	181}
	288}	57.5}	260}
	451}	54.6}	425}
61	287}	25.1}	410*}
	451}	69.2}	575*}
62	451	40.3	524
63	451	21.5	400*
64	143}	17.0}	318*}
	287}	61.7}	247}

*Interpolated from curves "Graphitization at Constant Temperature," H. A. Schwartz, TRANSACTIONS, American Society for Steel Treating, Vol. 10, p. 53, 1926.

half of the available carbon as graphite. From this it follows that if T be the time in hours to precipitate x per cent of the available car-

bon as graphite and T' be the time in hours to precipitate 50 per cent of the carbon,

$$\frac{T}{T'} = .3 + 0.014x$$

$$T' = \frac{T}{.3 + .014x}$$

from which T' may readily be calculated with sufficient accuracy having in mind the uncertainties in determining x .

It will be noted that particularly at 700 degrees Cent. (1290 degrees Fahr.) and also particularly in some of the alloyed metals, graphitization seems to progress not at all for many hours and then to accelerate greatly. The phenomenon has previously been observed.⁶ It has been discussed elsewhere as a high temperature phenomenon by the present author.⁷

The great delay in starting the reaction suggests a possibly needed correction to our original concept of the form of the graphitization curve concerning which more anon. The above method of interpolation seems better under the circumstances than the evaluation of a curve reconstructed to conform to the

$$c = a t^{\frac{2}{3}}$$

relation. It may even so be subject to some criticism which can be avoided only where two points, one slightly greater and one slightly less than 50 per cent completion are available.

From Table V by averaging the values for the final combined carbons on alloys 11, 21, 31, 41 and 51, none of which contain unusual elements, we find that the carbon solubility is almost exactly 1 per cent at 900 degrees Cent. (1650 degrees Fahr.). By inspection it is plain that this solubility was not increased by the presence of manganese, molybdenum or vanadium. The chromium alloy could not be heat treated long enough to attain equilibrium before decarburization became rapid and the results are therefore inconclusive. The form of curve as plotted from the data of Table II is consistent with, at most, a slight increase of solubility with increasing chromium.

For the purpose of further calculation it is assumed that the alloying elements present do not alter the solubility of carbon by amounts significant in comparison with the uncertainties of observation.

Table V does not yield any accurate information as to the effect

⁶Schüz and Stutz, "Der Temperguss," Springer, p. 58, Fig. 42, 1930.

⁷H. A. Schwartz, H. H. Johnson and C. H. Junge, "Some Transient Phase Changes During the Graphitizing Reaction, TRANSACTIONS, American Society for Metals, Vol. 24, September 1936, p. 551.

of alloying elements on the solubility of carbon in alpha iron. The samples which retain combined carbon even after hundreds of hours do not differ in appearance particularly from any underannealed malleable and one need not regard the residual carbides as anything but cementite. Malleable irons containing no visible carbides frequently contain by difference between total and combined carbon about 0.08 per cent combined carbon, a point worthy of detailed study. Quite likely but little more agraphitic carbon is actually in solution than in normal malleable although this conclusion could be proved only by observing the complete ultimate disappearance of cementite which seems to take prohibitively long. If, then, we calculate graphitizing time, assuming the insolubility of carbon, this is purely an expedient not supported by any proof of validity.

With the assumption that the solubility of carbon at 900 degrees Cent. (1650 degrees Fahr.) is always 1 per cent and at 700 degrees Cent. (1290 degrees Fahr.) always zero, we may, from Tables I, II and III, construct the following table of percentage (near 50) of completion vs. time and the corresponding calculated values for 50 per cent completion.

It is at once evident that there are, as might be expected, considerable uncertainties in the determination of graphitizing time. More particularly, material 42, which is a graphitizable steel rather than a cast iron, seems quite erratic. One must not lose sight of the fact that in this and its companion, 41, the conditions are very different from those for which the graphitization laws were deduced. For the present the data on these alloys may be regarded as illustrative only. Comparing the times from Tables IX and X for alloyed and unalloyed pairs, we obtain the following.

Table XI
Effect of Stated Amount of Alloying Element on Graphitizing Time Factor
by which Time is Increased

Designation	Element	Added Amount	900 Deg. Cent.	700 Deg. Cent.
11 and 12	Cr	0.30	2.0	250.0
21 and 22	Mn	0.45	0.3	1.0
31 and 32	Mn	0.51	2.0	7.0
51 and 52	Mo	0.27	1.5	..
51 and 53	Mo	0.65	4.5	..
51 and 50	V	0.17	2.0	..
61 and 62	Mo	0.23	1.5	1.0
61 and 63	Mo	0.45	1.5	1.0
61 and 64	V	0.14	..	0.6

In some instances, especially at 700 degrees Cent. (1290 degrees

Fahr.) the lack of effect of alloys is surprising and we are led to re-examine the form of the graphitization curves. In Fig. 1 the logarithm of the fraction of the original agraphitic carbon remaining ungraphitized is plotted against time. The heavy horizontal line marks the concentration below which these loci should be straight and above which they should be curved (convex upward) according to previously accepted opinion. They may be interpreted as straight to much higher concentrations of combined carbon than expected though this furnishes no conclusive proof, for the curvature would be only slight up to considerable concentrations.

If we choose to interpret Fig. 1 as differing only through experimental error from loci consisting of straight lines intersecting the line $\log 1 (=0.0)$ at various places representing various incubation times we get some such series of data as tabulated in Table XII.

Alloys may affect graphitizing rate either by altering the mean migratory distance of the carbon atoms, which is a reciprocal function of the number of nuclei per unit volume or by altering the rate of migration. One may separate the two mechanisms for if migratory distance were the only factor then graphitizing time would vary in-

Table XII

Designation	Incubation Time (hrs.)	Coefficient of Reaction Rate $d(\log C_0 - \log C)$
		$d T$
11	100	0.0080
12	100	0.0006
21	340	0.0030
22	40	0.0007
31	150	0.0020
32	350	0.0006
41	40	0.0013
42	40	0.0007
61	250	0.0030
62	250	0.0020
63	350	0.0015
64	100	0.0016

C_0 = initial agraphitic carbon in per cent, C = agraphitic carbon at time, T , in per cent, T in hours.

The tabulated values have meaning only to the extent that the underlying postulate is valid.

versely as the cube root of the number of nuclei per unit volume or graphitizing rate directly as this cube root. The product of graphitizing time and cube root of nuclear number would thus be constant if all else remained unchanged and if not constant, this product varies inversely as the migratory rate. In the following Table XIII the relative migratory rate so computed is plotted. The fundamental data

are found in Tables VI, IX, and X. It will be seen in Tables VII and VIII that generally there is a very large number of very small nuclei. It seems reasonable that if these are, as seems to be the case, so far incapable of growth that in the aggregate their great number does not account for any considerable amount of graphite, these should be omitted from the count. Table XIII is computed separately from both the total count and neglecting the smallest size.

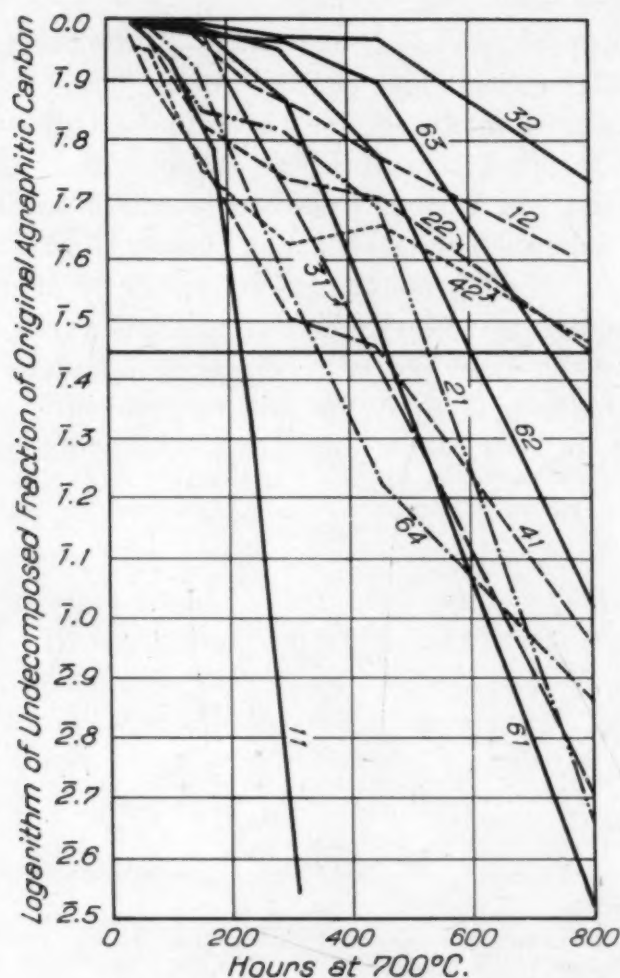


Fig. 1—Logarithm of the Fraction of the Original Agraphitic Carbon Remaining Ungraphitized Plotted Against Time.

Any attempt to correlate nucleus counts with the graphitizing rates below A_1 as interpreted in Table XII would seem to lack meaning for the logarithmic form of curve postulated there probably represents the reaction velocity of a mono molecular reaction and hence a process where velocity has nothing to do with migratory rates.

From Tables VI, VII, VIII and XIII we may compute the ef-

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Table XIII
Relative Migratory Rate

Temperature Designation	Computed from Total Number of Nuclei		Number of Nuclei of Significant Size	
	900 Degrees Cent.	700 Degrees Cent.	900 Degrees Cent.	700 Degrees Cent.
11	316	9.0	455	13.7
12	164	0.27	246	0.51
21	110	0.15	110	0.18
22	127	0.15	295	0.17
31	61	0.42	148	0.42
32	31	0.20	69	0.40
41	71	0.69	141	1.01
42	41	0.62	72	0.37
51	309	...	394	...
52	122	...	308	...
53	123	...	123	...
54	177	...	271	...
61	...	0.62	...	0.62
62	...	0.68	...	0.68
63	...	0.80	...	0.80
64	...	0.98	...	0.98

fects of the various alloying elements on the nuclear number and migratory rate by calculating the ratios of these constants for the alloyed and unalloyed specimens of each given pair.

The results will differ slightly accordingly as we take the total number of nodules or omit those which do not grow. A separate comparison must also obviously be made for 900 and 700 degrees Cent. (1650-1290 degrees Fahr.). In Table XIV below a value greater than unity indicates that the constant in question is numerically greater in the absence of the alloy, a value less than unity that it is greater in the presence of the extra element.

Table XIV
Effect of Alloying Elements on Nuclear Number and Migratory Rate

Temperature Constant Designation	Element	Conc. Per Cent	Nodules Counted	900°C		700°C	
				No.	Rate	No.	Rate
11 }	Cr	0.30	all	1.4	2.0	0.4	333
12 }			sig. only	1.6	1.8	0.7	268
21 }	Mn	0.45	all	0.035	0.9	0.8	1
22 }			sig. only	0.45	0.4	0.6	1
31 }	Mn	0.51	all	0.64	2.0	2.4	2
32 }			sig. only	0.80	2.1	19.0	1
41 }	Mn	0.52	all	0.95	1.7	0.7	1
42 }			sig. only	0.069	2.0	0.4	2.7
51 }	Mo	0.27	all	2.6	2.5
52 }			sig. only	2.0	1.3
53 }	Mo	0.65	all	5.2	2.5
54 }			sig. only	2.5	3.2
61 }	V	0.17	all	1.8	1.8
62 }			sig. only	3.1	1.5
63 }	Mo	0.23	all	1.6	0.9
64 }			sig. only	1.6	0.9
65 }	Mo	0.45	all	1.1	0.8
66 }			sig. only	1.1	0.8
67 }	V	0.14	all	0.7	0.6
68 }			sig. only	0.7	0.6

If we choose to interpret graphitization below A_1 in the light of Fig. 1 we may construct Table XV showing the effect of the elements on incubation time and subsequent graphitizing rate, the effect being computed, as before, as the ratio of the constant for the unalloyed metal divided by the constant for the alloyed metal.

Table XV
Effect of Alloying Elements of Incubation Period and Graphitizing Rate
at 700 Degrees Cent.

Designation	Element	Concentration	Incubation Period	Rate
11-12	Cr	0.30	1.6	15
21-22	Mn	0.45	8.5	4
31-32	Mn	0.51	0.4	3
41-42	Mn	0.52	1.0	2
61-62	Mo	0.23	1.0	1.5
61-63	Mo	0.45	0.7	2.0
61-64	V	0.14	3.5	1.0

SUMMARY

The very nature of the present investigation makes rigidly quantitative treatment impossible. No organization could hope to have time for a sufficient number of repetitions of the experimentation to wipe out all the intangible variables. Generalizing from the data available is, therefore, to some extent a matter of judgment rather than calculation. Particularly, the treatment of the smallest sized nodules is always open to question.

One notes first that even the unalloyed irons differ greatly in nuclear number. In the present investigation there is less difference in nuclear number in these irons germinated at 900 and 700 degrees Cent. (1650-1290 degrees Fahr.) than was expected. Contrary to the earlier observations in the references, the nuclear number is not systematically less in metal made in the electric furnace than in that made in the reverberatory furnaces. The nuclear number in the electric furnace iron of about $2\frac{1}{2}$ per cent carbon is greatly lower at 900 degrees Cent. (1650 degrees Fahr.) and greatly higher at 700 degrees Cent. (1290 degrees Fahr.) than in alloys having a lower carbon content near the limit of solid solubility.

The present investigation is far too brief to provide an explanation of the causes of these phenomena. We merely record the facts. The alloys seem to be without effect on the form of graphite as defined by its density of packing.

It appears that manganese added to (electrically melted) alloys

increases the nodule number, germination being at 900 degrees Cent. (1650 degrees Fahr.), while chromium, molybdenum or vanadium added to (fuel melted) alloy consistently decrease the nodule number. The observation seems very significant. One cannot say whether manganese is unique in its behavior or whether electric furnace metal is per se different from reverberatory metal.* The latter explanation seems the more plausible but the point certainly merits further study, and experiments are in progress to clarify the matter. Some of the observations at 700 degrees Cent. (1290 degrees Fahr.) are a bit erratic, but the addition of alloys seems to alter the nuclear number, germination at 700 degrees Cent. (1290 degrees Fahr.), materially. The 2.15 carbon-manganese alloy may be an exception if the results are reliable.

The addition of alloys, except chromium, seems to alter the migratory rate of (atomic?) carbon in alpha iron distinctly, but not greatly. Chromium, however, retards migratory rate immensely. All the elements retard carbon migration (atomic or as Fe_3C ?) in gamma iron except in the case of manganese and 2.45 per cent carbon. The retarding effect seems in some degree to increase with the amount of the alloy present. The amount of retardation is about equal for 0.3 per cent chromium, 0.5 per cent manganese, 0.3 per cent molybdenum and 0.2 per cent vanadium. The four elements do not, therefore, differ very greatly among themselves in the quantitative effect on carbon migration. In Fig. 2 the data for the effect of elements on migratory rate at 900 degrees Cent. (1650 degrees Fahr.) from Table XIV have been plotted on a semi-logarithmic scale. Considering only nodules capable of growth, a relation approaching the rectilinear is observed. Should one consider that the retardation depends more on how many stranger atoms exist in the gamma iron lattice than on what these strangers are?

From the conditions set forth in Fig. 1 one is tempted to consider that below A_1 the reaction is one of the first order, thus not being dependent upon nodule number for a determination of its rate. Although the present paper lends support to such a view, this conclusion should be approached with caution for other facts are known which contradict it.

Treating Fig. 1 as having only empirical significance, we find

*Since the preceding was written, an addition of manganese to fuel melted metal was observed to decrease the nodule number in specimens germinated at 900 degrees Cent. (1650 degrees Fahr.). The increase observed in electrically melted metal is thus apparently a peculiarity of the melting method and not of the element manganese.

that again chromium very greatly retards the graphitizing reaction below A_1 but vanadium is without effect. Manganese seems to retard more actively the higher the carbon and molybdenum is somewhat less active than a similar amount of manganese.

Observing the effect of vanadium on incubating time, one is led to interpret the effect of that element at 900 degrees Cent. as a sim-

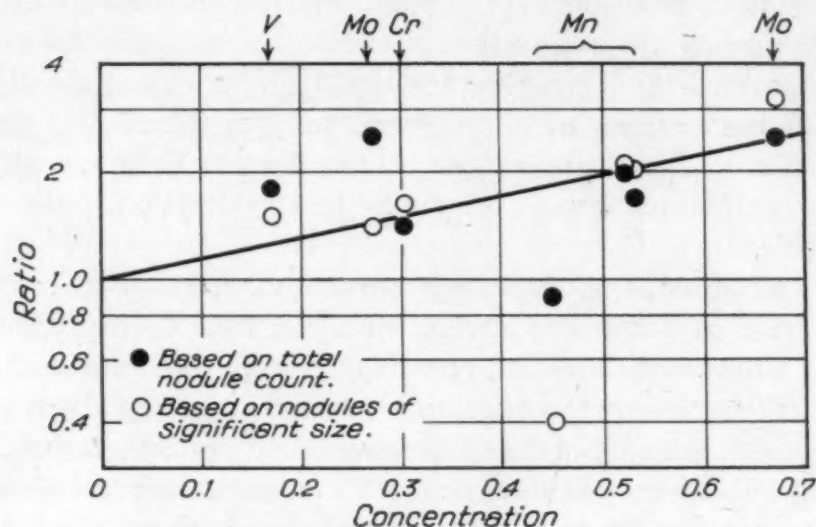


Fig. 2—Effect of Elements on Migratory Rate at 900 Degrees Cent. Plotted on Semi-Logarithmic Scale.

ilar increase in the time before the reaction begins. The data fit rather well into this premise. On the whole, we are again led to consider how complex is the entire graphitizing phenomenon. However disappointing, it is not surprising that one cannot fit the quantitative data into a well defined pattern conforming rigidly to a few simple basic assumptions. It appears that the effect of an element on graphitization is made up of two parts, an effect on nucleus number and one on migratory rate. The former may in turn be also a function of the method of preparation of the metal and of addition of the alloy. Under these circumstances one should be cautious in expressing his observations, reliable though they may be in the form of general conclusions. Furthermore, although this paper does not touch upon the point, the metal may not be homogeneous in alloy content, especially as between the cementite and austenite phases. The following, however, are probably justified.

CONCLUSIONS

Within the range of elements and concentrations here investi-

gated, the following conclusions are offered applicable only under the present experimental conditions.

(1) It is not yet possible to predict from a knowledge of melting conditions and composition, the number of nuclei which will grow into carbon nodules on germination, even in unalloyed irons.

(2) It is unlikely that useful data as to the effect of alloys on graphitization rates can be obtained unless a comparison is possible with unalloyed metal made under exactly the same conditions.

(3) The retarding effect of the elements chromium, manganese, molybdenum and vanadium on the graphitizing reaction is confirmed (with one exception in the case of manganese and fairly high carbon).

(4) The addition of manganese increases the number of nuclei capable of growth at 900 degrees Cent. (1650 degrees Fahr.) while the addition of the other three elements reduces this number. Later work has shown that the peculiar behavior of manganese additions is due to the melting method and that manganese added to metal similar to that to which chromium, vanadium and molybdenum were added decreases the nodule number.

(5) The addition of the elements is without large effect on the number of nuclei capable of growth at 700 degrees Cent. (1290 degrees Fahr.).

(6) The migratory rate of carbon in gamma iron is retarded by all the elements, presumably to a degree related to the amount of the alloying element.

(7) The effect of all four elements on migratory rate in gamma iron is of a similar order of magnitude.

(8) The migratory rate of carbon in alpha iron is greatly retarded by chromium and little affected by the other elements.

(9) The retarding effect of manganese on graphitization below A_1 seems to depend markedly on the carbon content.

(10) The solubility of graphite in gamma iron is not materially affected by the alloying elements.

(11) Alloys do not greatly affect the sprawliness of the graphite.

DISCUSSION

Written Discussion: By H. L. Anthony, 3rd, research metallurgist, The Midvale Co., Philadelphia.

This paper is of particular interest in view of some recent work done by the writer in regard to graphitization of white cast iron below the A_1 point.

Most of this low temperature study was confined to unalloyed irons, with the exception of one composition which contained 0.50 per cent nickel.

No doubt, the authors have been very careful in their melting procedure, but such points as analogous melting scrap, method of melting, maximum bath temperature, the order of alloying additions and pouring temperatures are vital steps in the procedure to obtain alloys for direct comparisons. With such variables to contend with, it is difficult to arrive at definite facts which would apply universally, even to similar compositions.

Very little information exists as to the effect of chromium, manganese, vanadium and molybdenum in commercial percentages on the reaction velocity and migratory rates of graphitization below the A_1 point. In this respect, the authors present entertaining data.

In Table II, the graphite formed at 900 degrees Cent. (1650 degrees Fahr.), from composition 12, follows the straight line relationship, while the same composition at 700 degrees Cent. (1290 degrees Fahr.) reacts very sluggishly, as do the rest of the compositions at this temperature. This character of reaction has been confirmed by the writer with unalloyed compositions when the graphitization was undertaken at 650 degrees Cent. (1200 degrees Fahr.). The writer has found that complete graphitization of unalloyed white cast iron can be accomplished in 384 hours, and this figure only compares to the authors' 50 per cent graphitization in Table X.

From the data in Table VI, it would appear that the number of graphite nodules per cubic millimeter, formed at 700 degrees Cent. (1290 degrees Fahr.), were influenced to a large extent by the method of melting. For example, compositions 21, 22, 31, 32, 41 and 42 were melted in an electric furnace and show a high nodule count, while compositions 61, 62, 63 and 64 were melted in a fuel-fired furnace and exhibit a low nodule count. Therefore, it seems that the electric method of melting has a large influence on the graphitization of nuclei.

The writer has used the Schneidewind* method of nodule count for temperatures of 650 degrees Cent. (1200 degrees Fahr.) and the two-stage anneal starting at 920 degrees Cent. with unalloyed bars from the same heat.

Table I contains the nodule count by this method:

Hours at 650 Degrees Cent.	Graphite Nodules 3½ x 4½ Inches x 55 Diameters
24	None
48	None
72	14
98	89
122	128
146	167
176	169
201	170
201-324	168-175

Two-stage annealing at 920 degrees Cent. (1690 degrees Fahr.) produces 61 nodules.

From Table XI, compositions 51 and 53, with 0.65 per cent molybdenum, would appear to have the same increase of time factor as compositions 11 and 12, which contain 0.305 per cent chromium. It would have been of consider-

*"The Malleabilization of White Cast Iron," Engineering Research Bulletin No. 24, August 1933, University of Michigan.

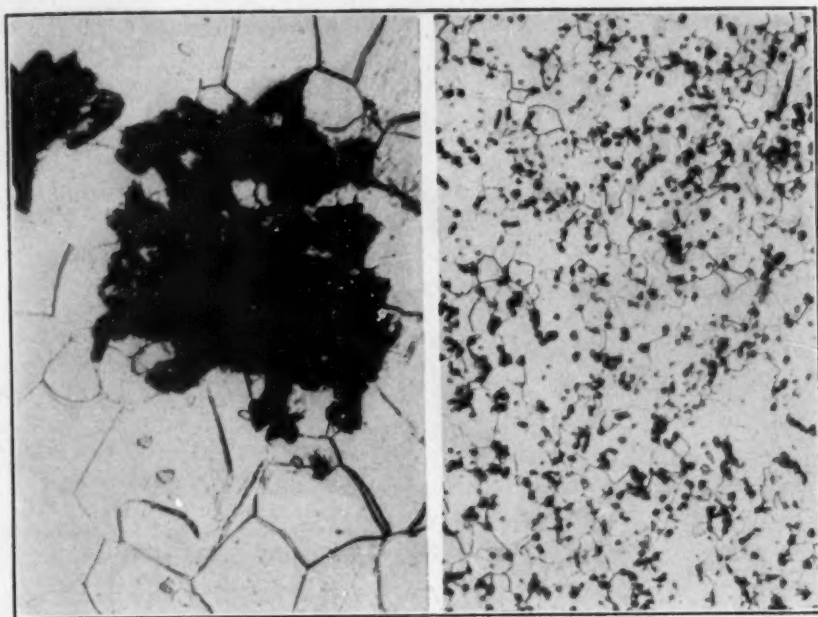


Fig. 1—Malleable Cast Iron Produced by Heating at 920 Degrees Cent. (1690 Degrees Fahr.) for 20 Minutes, Water-Quenched and Then Reheated at 650 Degrees Cent. (1200 Degrees Fahr.) for 168 Hours. Photomicrograph at the Left is From the Same Bar, But it Received a Two-Stage Commercial Anneal from 920 Degrees Cent. (1690 Degrees Fahr.). Both Photomicrographs are $\times 400$, Etchant Nital.

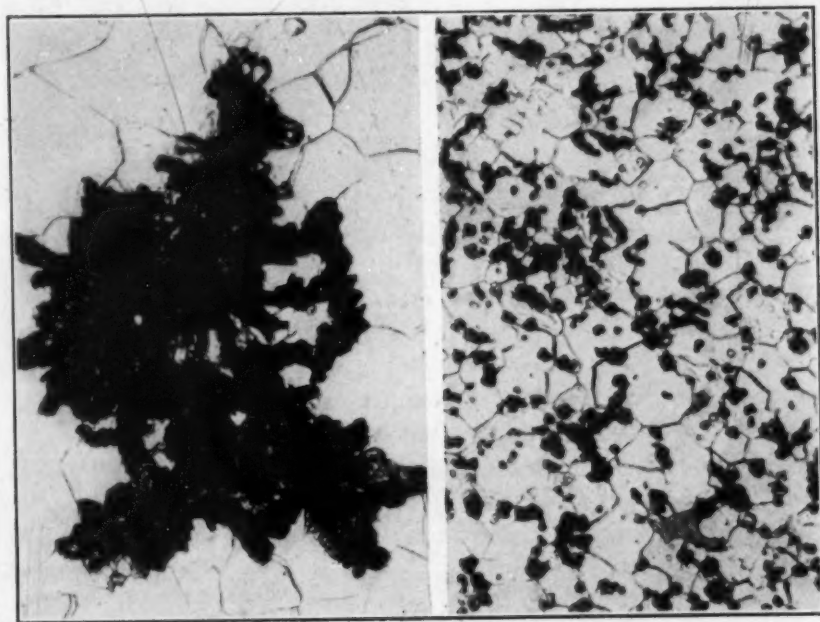


Fig. 2—Malleable Cast Iron Which Was Heated for 20 Minutes at 920 Degrees Cent. (1690 Degrees Fahr.), Water-Quenched, Reheated at 650 Degrees Cent. (1200 Degrees Fahr.) for 30 Hours and Then Finally Given a Commercial Anneal from 920 Degrees Cent. (1690 Degrees Fahr.). Each at $\times 400$, Etchant Nital.

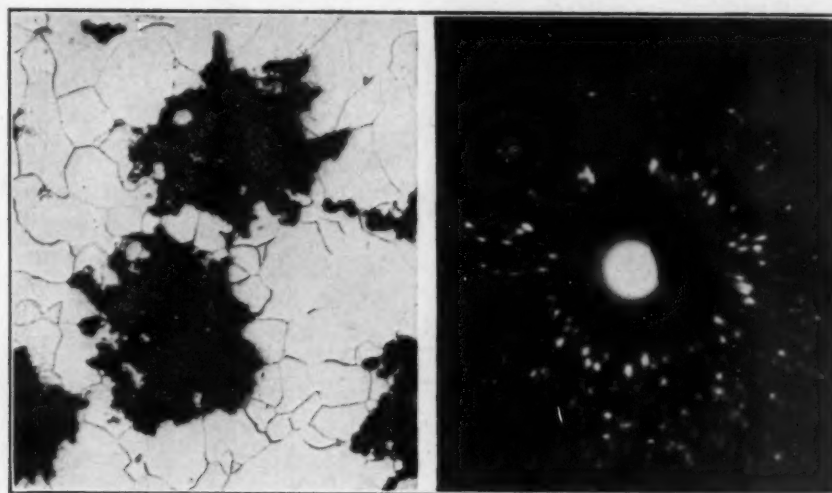


Fig. 3—Malleable Cast Iron ($\times 150$) Produced by Commercial Annealing with the Corresponding Monochromatic Pin-Hole Picture Taken with a Chromium Target at 5 Centimeters Distance. Two Hours Exposure.

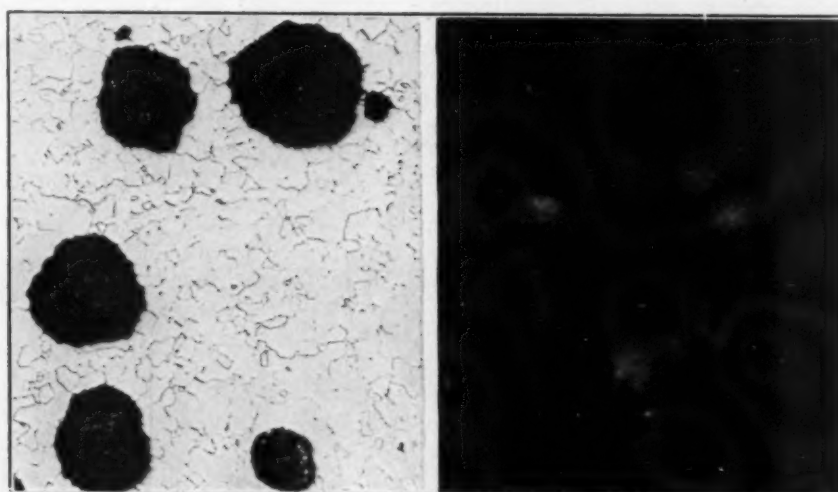


Fig. 4—Low Temperature Malleable Cast Iron Produced by Heating at 650 Degrees Cent. (1200 Degrees Fahr.) for 16 Days ($\times 150$) with Corresponding Monochromatic Pin-Hole Picture Taken with a Chromium Target at 5 Centimeters Distance. Exposure 2 Hours.

able value to have had the time factor for 51 and 53 at 700 degrees Cent. (1290 degrees Fahr.) for this higher amount of molybdenum.

In view of the interest concerning the germination of nuclei and graphite nodule count, the writer would like to present Figs. 1 and 2, which contain photomicrographs of a nickel cast iron of the following composition:

	Per Cent
Carbon	2.54
Manganese	0.30
Silicon	0.97
Nickel	0.50

The photomicrographs at the left of Figs. 1 and 2 are of the same com-

position, but they have been annealed from 920 degrees Cent. (1690 degrees Fahr.) in two stages and are illustrated as in method of comparison.

In the photomicrograph at the right of Fig. 1 is shown the size and distribution of graphite nodules in a $\frac{3}{4}$ -inch round heated for 20 minutes at 920 degrees Cent. (1690 degrees Fahr.), water-quenched and subsequently reheated to 650 degrees Cent. (1200 degrees Fahr.) for 168 hours. It seems evident by starting out with carbide (or carbon) in a small particle size, such as in the martensitic condition, very small nodules of graphite result when complete graphitization is carried out at 650 degrees Cent. (1200 degrees Fahr.).

A similar specimen of the same composition as in Fig. 1 was heated for 20 minutes at 920 degrees Cent. (1690 degrees Fahr.), water-quenched and reheated at 650 degrees Cent. (1200 degrees Fahr.) for 30 hours, after which it was given a commercial two-stage anneal from 920 degrees Cent. (1690 degrees Fahr.). The microstructure after this treatment is illustrated in the left of Fig. 2.

Apparently after the incubation period of 30 hours at 650 degrees Cent. (1200 degrees Fahr.) the already formed nuclei persisted after heating above the A_1 point. Such an existence is likely since the agraphitic carbon will enter solution much more rapidly than the already formed nuclei. Consequently, these low temperature nuclei then act as high temperature nuclei and graphitization then proceeds about these points.

Perhaps it would be of interest to the authors to treat their compositions as outlined in Figs. 1 and 2 in order to ascertain what effect this type of treatment might produce in number, maximum diameter and density of packing of graphite nodules.

Another aspect of study pertaining to graphitization below the A_1 point is illustrated by means of monochromatic pin-hole pictures of commercial malleable and malleable produced at 850 degrees Cent. (1560 degrees Fahr.) which might be of some significance. Fig. 3 illustrates the ordinary type of malleable cast iron with the corresponding monochromatic pin-hole picture which discloses large grain ferrite of random orientation. On the other hand, Fig. 4 is malleable produced at 650 degrees Cent. (1200 degrees Fahr.) and the monochromatic pin-hole picture reveals the evidence of small grain, some strain and perhaps preferred orientation. However, the writer only presents these two figures as matter of interest for future endeavor along the lines of low temperature graphitization.

In conclusion, it is hoped that the authors will present at some future time their final results in respect to the influence of manganese on the final nodule count for electric and fuel melting methods.

Written Discussion: By R. Schneidewind, research engineer, University of Michigan, Ann Arbor, Michigan.

The authors present one of the first theoretical attacks on the problem of the effects of alloys on graphitization of white irons. The method of graphite counts and the mathematical approach must have entailed an enormous amount of difficult and tedious work and the authors should be complimented on their results.

We agree that the results must be considered in the light of trends rather

than as a generalization of the quantitative retarding effects of the alloys studied. For example in Table XI it was found that 0.17 per cent vanadium increased the time necessary for graphitization at 1650 degrees Fahr. (900 degrees Cent.) twofold. In electric furnace heats of irons of the same general composition, we found that the plain iron had completely graphitized at 1700 degrees Fahr. (925 degrees Cent.) in 7 hours whereas the iron containing 0.15 per cent vanadium after 24 hours still had an unbroken network of cementite although some graphite had formed. These differences are undoubtedly due to differences in melting procedures and raw materials.

In some fragmentary work done on pearlitic irons for brake drums we found that raising the manganese content from 0.5 to 0.9 per cent had no appreciable effect upon graphitization at 1700 degrees Fahr. (925 degrees Cent.) but that some retardation was noticeable below the critical temperature.

Could the authors explain why it is desirable to calculate the 50 per cent completing point of graphitization as shown in Table X. The method of calculation is ingenious but would it not be of more practical value to calculate the 100 per cent or the 95 per cent completion point.

In Table XI the coefficient of reaction rate is evidently calculated on the assumption that the solubility of carbon in alpha iron is zero. These values, however, represent the slopes of the straight portions of the lines in their

Fig. 1. The slope of the curves is $\frac{d(\log C - \log C_0)}{dT}$ and is a negative number. Has the coefficient been multiplied by -1 to make it read

$\frac{dT}{d(\log C_0 - \log C)}$ as shown simply in order to be a positive number?

The authors discuss the delay in starting the graphitizing reaction which they term the germination period. In this they are in full agreement with the dilatometer results of Kikuta and of Sauveur. Work done at the University of Michigan in which the progress of graphitization was measured by chemical analyses and by microscopic examination did not bear out this behavior especially above the critical temperature.

Although it is generally accepted that alloys such as chromium retard graphitization, it should not necessarily follow that the alloys retard the rate of atomic carbon migration in gamma iron. The rate of carbon migration is most probably determined by the medium through which it travels, gamma iron, and the kinetic energy in keeping with the temperature of annealing. Carbide forming alloys, especially in the quantities used in white iron, cannot appreciably affect the nature of the gamma iron. The retardation of graphitization can, however, be explained by the following probable effects of the alloys.

1. Stabilization of the carbide.
2. The formation of fewer graphite nuclei and hence increasing the mean migratory distance for the carbon atoms.

Oral Discussion

O. E. HARDER:¹ I want simply to ask a question regarding this paper. This

¹Assistant Director, Battelle Memorial Institute, Columbus, Ohio.

relates to the possible influence of hydrogen in the metal at the time of solidification. I am wondering if the authors have studied this relation. I am wondering, also, if the findings with reference to the effects of the metals which they have studied, may, to some extent, at least, have been influenced by the possible effects of those elements on the hydrogen dissolved in the metal at the time it was melted, and the hydrogen released during solidification.

Authors' Closure

By H. A. SCHWARTZ

We are much interested in Dr. Anthony's constructive discussion of our paper. We are in the main apparently pretty much in agreement with most of the discussor's comments. Perhaps the most important difference of opinion would reside in the use by Dr. Anthony of data based on Schneidewind's method of counting nodules. It is our opinion that this method is mathematically unfounded and that calculations based upon it are so unreliable that we would disregard any conclusions from data based upon it.

We have already pointed out in our paper that the difference in melting conditions is of enormous consequence in determining the nodule number. We would prefer melting conditions and not merely say that this is due to electric melting as Dr. Anthony puts it. It is merely speculation, but our opinion is that it is more a question of furnace atmosphere than of heat source. The reference to Schwartz and Ruff will give some reasons for this belief.

We have recognized and emphasized in our paper that in investigations of this kind it is necessary to compare material in which all of the variables except that under consideration remain as nearly constant as possible. We have attempted to maintain this constancy as nearly as was possible and have described as completely as we know how what our conditions were. We are certainly in accord with the commentator that these results cannot necessarily be transferred to other perhaps unknown conditions. The desire to attain constancy of melting conditions was one of the reasons for making certain melts in the electric furnace. This procedure chanced to give us a lead on another important variable.

The paper would be more coherent if we had made the manganese additions in the same manner as the others. A further investigation of manganese to fuel fired furnace metal was carried out after the paper was written but too late for including the data. We have now added some further material in the tables of the text which, however, has not been carried over into the calculations of the body of the paper.

It is to be understood that in these alloys the intention was to proceed in the same manner as for the chromium, molybdenum and vanadium alloys. The metal was made several months later, however, and it is therefore less certain that the raw materials used were identical.

Certain omissions referred to by Dr. Anthony are due to the fact that we know of no acceptable method for evaluating some groups of data for graphitizing rate.

We have in the past observed the finer nodule number in quenched material and discussed it in "Graphitization of Prequenched White Cast Iron," Schwartz,

Johnson and Junge, TRANSACTIONS, American Society for Steel Treating, Vol. 17, 1930, p. 383.

The X-ray data given by Dr. Anthony form an interesting addition to our general knowledge without apparently being intended to have any direct connection with the subject of the present paper.

With regard to the discussion kindly furnished by Dr. Schneidewind we may say that consultation of the third reference of our paper will explain that the relative graphitizing rate computed at fifty per cent completion is the same as that which would be obtained at any other per cent. The merit of working at fifty per cent is that this point can be sensitively determined. The reasoning underlying this conclusion forms a major portion of the reference and is far too voluminous to repeat in detail.

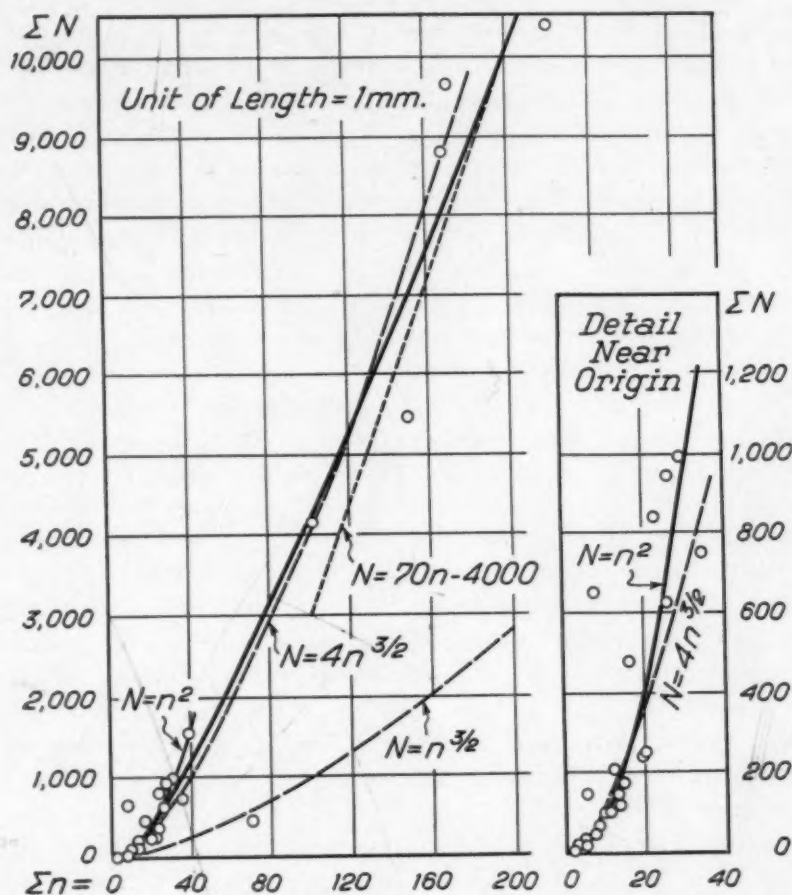
Dr. Schneidewind is quite correct in his interpretation of the headings of Fig. 1. We did not deem it a matter of any particular importance what the sign of the rate of change of carbon was with respect to time since the metallurgical reader obviously recognizes that combined carbon decreases or graphitic carbon increases with time. If the letters *c* of the equation are read for graphitic carbon, one sign would have to be used, if for available combined carbon the other.

We cannot refrain at this time from again recording our objection to the methods employed by Dr. Schneidewind originally and now quoted by Dr. Anthony for proceeding from the number of nodules per unit area to the number of nodules per unit volume. This author has not before him the original bulletin of the University of Michigan covering Dr. Schneidewind's work. Some familiarity with the matter, however, causes him to believe that the Schneidewind reasoning is that from a number of nodules observed per unit area one can imagine the area subdivided in units each dominated by one nodule and can imagine these to be the square cross section of cubes. If then one considers the three dimensional extension of these cubes he finds that the volume dominated per cube is the cube of the square root of the area dominated by the nodule. It would seem to follow that the number of nodules per unit volume should be the number per unit area raised to the three-halves power.

The accompanying figure reproduced with some modifications from "A Simple Approximate Method for Determining Nodule Number," *Metals and Alloys*, Vol. 7, No. 11, November 1936, shows the actual number of nodules per unit area and per unit volume computed for thirty-one alloys, mainly those of the present paper. For comparison there has been shown a dot and dash line corresponding to the three-halves power relationship. This evidently in no wise approximates the figures. The curve, $N = 4 n^{3/2}$ has been drawn in by inspection and represents moderately well the observed points. It corresponds to four times what the writer understood to be Dr. Schneidewind's assumption as to the number of nodules per unit volume.

It may be worthy of note that the coefficient 4, here arrived at entirely empirically, bears at least a rough relation to the ratio of the diameter of the sphere circumscribing the precipitated graphite to the length of the cube edge containing the remainder of the alloy. This relationship has not been checked up in detail but if it exists it represents the chance of cutting some portion of the graphitic nodule by a plane intersecting the parent cube at random par-

allel to one of its sides. The calculation takes into account the amount of precipitated graphite and the density of packing. If the foundation for the coefficient 4 is as indicated, then the coefficient will vary as graphitization increases and with any factors altering the density of packing. Since the



present samples were all selected to be moderately complete so far as the graphitizing reaction is concerned, the coefficient may have attained some semblance of constancy. A further investigation of the details would certainly be not without interest.

In view of the experimental demonstration that Dr. Schneidewind's assumptions unmodified are in error as to the number of nodules per unit volume in the ratio of about 1 to 4 we cannot effectively discuss any conclusions based on his assumptions except where relationships are involved which would cancel out this coefficient. Where the coefficient does cancel out, conclusions based on his method of counting yield accurate results.

We follow Dr. Schneidewind's comment, a small amount of chromium cannot greatly affect the nature of gamma iron, quite well. We do not understand so well the remainder of his related comments. Dr. Schneidewind apparently agrees that chromium may affect graphitizing rate by varying the number of nuclei. It is of course conceivable that the nucleus number decreases so far that even an increased migratory rate would still involve a

decreased graphitizing rate. It was our purpose in presenting the paper to attempt to separate these two phenomena. In this purpose we were successful to the extent of assigning a quantitative value to the two items separately. If the implication is that we said *a priori* that chromium should have any particular effect upon migration rate, that was not our purpose nor do we think that we inadvertently gave this impression.

Dr. Schneidewind's reference to "kinetic energy in keeping with the temperature of annealing" is too vague for us to follow what he has in mind. We would point out, however, that if graphitization is retarded by lowering the rate at which the carbide, massive or in solution, can decompose, then there would cease to be that relation between graphite and time which corresponds to a reaction in which the rate is controlled by the ability of the carbon to migrate to the nodules formed. If this condition should be set up then the number of nodules available per unit volume for the deposition of graphite is no longer the controlling factor in altering graphitizing rate. It is our understanding that Dr. Schneidewind feels that it generally is such a controlling factor. We are unable to visualize any mechanism for the graphitizing reaction in which its rate is dependent upon nodule number in which it would not also be dependent on migratory rate. We would regard it as a matter for experimental verification to determine whether the presence of alloying elements could or could not alter this rate. If it does alter it, it certainly cannot do so by anything it does to a carbon atom; however, perhaps the carbon does not migrate as an atom or if it does perhaps a carbon atom finds it more or less difficult to leave the vicinity of a chromium atom than an iron atom. For the purpose of the present paper we would prefer not to attempt to defend any particular hypothesis.

We are unable to answer Dr. Harder's inquiries having taken no cognizance of the possible presence of hydrogen.

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